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Methods for the Direct Determination of Heavy-Metal Pollutants in the Environment.

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METHODS FOR THE DIRECT DETERMINATION OF HEAVY-METAL POLLUTANTS IN THE ENVIRONMENT

A Dissertation

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Duane Kent Wolcott
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DEDICATION

TO:

Joanne Marie Moreau Wolcott

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Lastly, the author wishes to acknowledge the understanding and moral support of his spouse, who helped him maintain his sanity during a difficult period.

FOREWORD

A selection of work appearing in this Dissertation has been published in the following papers:

1. "Nonflame Atomic Absorption in the Vacuum Ultraviolet Region; The Direct Determination of Mercury in Air at the 184.9 nm. Resonance Line", J. W. Robinson, P. J. Slevin, G. D. Hindman, and D. K. Wolcott, Analytica Chimica Acta, 61, 431 (1972).
2. " Direct Determination of Cadmium in Air and Liquid Samples", J. W. Robinson, D. K. Wolcott, P. J. Slevin, and G. D. Hindman, Analytica Chimica Acta (in press).
3. "Calibration Techniques used in Direct Determination of Atmospheric Metallic Pollutant levels", J. W. Robinson, and D. K. Wolcott (in press)

The papers presented at the following meetings were based in part on work from this Dissertation:

1. "Continuous Monitoring of Metals in Air", J. W. Robinson, G. Hindman, P. Slevin, and D. Wolcott, 11th Annual Meeting of the Society of Applied Spectroscopy, Dallas, Texas, September 1972.
2. "Direct Determination of Cadmium in Air, Water, Seawater, and Urine", D. K. Wolcott, J. W. Robinson, P. J. Slevin, and G. D. Hindman, 28th Southwest Regional A.C.S. Meeting, Baton Rouge, Louisiana, December, 1972.

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ABSTRACT

Heavy-metal pollutants are usually present in the ecological biosphere, that is, the portion of the earth which supports life, at concentration levels lower than the direct measurement capability of most analytical techniques. Hence to determine the concentration of these pollutants requires the collection of large samples and/or a pre-analysis concentration step. The collection and pre-concentration not only require a great deal of time, but can introduce errors even in the hands of experienced analysts, not to mention inexperienced personnel. Hence, direct methods of analysis are preferred.

An instrument has been designed for the direct, real-time determination of heavy-metal pollutants by atomic absorption spectroscopy. The instrument used a carbon bed atomizer for the reduction of metal pollutants to free atoms, and a heated quartz long path absorption tube to maintain the atoms in the light path in the free atomic state. The tube served to increase the optical path available for absorption, thus increasing the sensitivity of the atomic absorption technique. The instrument, with only minor modification, has been found suitable for the direct determination of heavy metals in solid and liquid, as well as gaseous (atmospheric) samples.

The instrument was utilized for the direct determination of cadmium in the atmosphere, in seawater, in biological fluids, in filter papers, and in plastics. The effects of the operating

parameters of the atomizer, such as carbon size, depth of carbon bed, temperature, and air flow rate were studied. Both atomic absorption and molecular absorption were investigated, and it was found that the use of the carbon bed atomizer largely eliminated interferences due to molecular absorption.

Devices were developed for the calibration of the instrument for air analysis. These devices were investigated as to their operational characteristics at the very low injection levels (10^{-12}g) which were necessary for the analysis of the numerous samples studied. The problems associated with trace contaminants in the calibrating media were investigated and attempts made to eliminate the contamination.

I. INTRODUCTION

In recent years, there has been a great furore throughout the world over the impact of technological man and his activities upon the planetary ecology.[1] Attitudes about pollution have ranged between the extremes of total disregard of the consequences[2] to the prediction of the immediate disappearance of all life on earth.[3] The debate has extended into both the public and professional media, with bitter outbursts from each of the various factions involved. It is obvious to anyone who has ever visited a major city that there are definite pollution problems. But these problems have been with us in one form or another for ages. It is only recently, however, that the extent of the problem of pollution has become great enough to cause a resolution on a part of the general public to "do something about it." The question that immediately arises is , WHAT? The pollution problem involves so many interlocking factors, and our knowledge of these factors, both singly and together, is so absymal, that an overall, immediate, effective solution is just not possible.

Many of the more radical elements in our society have recommended a complete abandonment of all industrial and advanced technological activities and a return to an organic, agrarian economy with only "natural" products in use.[4] Apart from defining exactly what constitutes a natural product, and apart from the fact that even natural products cause pollution (ask any sanitary engineer), a world population of four billion people cannot be supported at a level much above starvation by an organic technology. There are

just not enough natural products to go around. It is, therefore, the duty of scientists, engineers, and politicians (everyone, in fact) to seek a solution which will not involve the disintegration of the living standards enjoyed by the peoples of the world. It is, in fact, their duty to solve the pollution problems while allowing the underdeveloped nations of the world to raise their living standards to an acceptable level.

Of the many aspects of environmental pollution, one of the most serious is the introduction into the environment of toxic materials, both natural and man-made, in ever-increasing quantities. The problem of man-made pollutants involves the formulation and introduction into the environment of chemicals not known to occur naturally, for example, DDT, polychlorinated biphenyls, arsenical pesticides, nerve gas, etc., which may have disastrous effects. The second factor, that of naturally occurring toxic materials, involves the accelerated introduction of these materials into the environment <u>via</u> their use in manufacturing processes. Examples are manifold: lead from automobile exhausts; mercury from industrial processes; cadmium from tires and electroplating; nickel, manganese, and iron in steel manufacture; nearly the periodic chart from coal combustion. All of these processes involve a change in the concentration of heavy metals in the biosphere, resulting in local "hot-spots" of heavy-metal pollution. This increase creates the possibility of a long-term increase in the concentration of heavy metals (relative to the present natural abundances) in the environment. Such increases may, in time, produce devastating biological results.

In order to solve the problems of toxic materials in the environment, it is first necessary to define them. What are the "natural" levels of naturally occurring toxic materials? Do the man-made toxic materials biodegrade? Are the products of degradation toxic or harmless? At what levels do harmful effects occur? All of these questions and others like them require the measurement of these toxic species as they are found in the environment. Quantitative measurements of chemicals in various systems have always been the unique forte of the analytical chemist. Physical chemists may elucidate the mechanisms of pollution, organic chemists may build bio-degradability into normally toxic materials, inorganic chemists may provide new means of chemical processing which reduce pollution. The analytical chemist must be a key factor in elucidating the chemical aspects of pollution before the other specialists can set about solving them.

Unfortunately, most of the analytical techniques currently available are insufficiently sensitive to measure the ultra-trace levels at which many pollutants are found in nature. The most sensitive of these methods demanded either a highly developed laboratory technique (for example: catalytic wet chemical methods[5], solvent-extraction concentration schemes[6]) or highly sophisticated and expensive instrumentation (i.e. spark source mass spectrometry[7], neutron activation analysis[8]). Even the available techniques were generally incapable of real-time analysis. It has been the goal of this research to try to devise methods with the

requisite sensitivity, improved simplicity, accuracy, and low cost.

One of the more sensitive and convenient tools for the quantitative determination of the metallic elements had been flame atomic absorption spectroscopy. The advantages of the technique have been adequately discussed,[9] and the technique represents an ideal solution to many of the problems of determining metallic pollutant levels in the environment. However for many other problems involving measurement of environmental metallic pollutants, the standard flame atomic absorption technique did not possess adequate sensitivity.

It was felt that the sensitivity of the atomic absorption technique was subject to great improvement. Although there were many areas in which improvements could be made: light sources of greater intensity[10], detectors of greater stability[11], double-beam methods[12], etc., the factor most likely to result in greatly improved sensitivity was in the method of producing free atoms.[13] The standard flame atomization techniques have been shown to be notoriously inefficient as a means of producing a stable population of free atoms.[14] To overcome this deficiency, attempts were made to increase the number of free atoms in the light-path. These attempts included multiple-pass optics[15], long-slot burners[16], and light-path extension adapters[17,18,19] which attempted to increase the cell length and hence the sensitivity. It was apparent that these approaches were insufficient to increase sensitivity of the flame atomizer enough to allow the direct, real-time determination of metals in the environment.

Concurrently with the development of the flame atomizer, B. V. L'vov demonstrated that it was possible to produce free atoms very efficiently without the use of a flame.[20] Unfortunately, the L'vov technique suffered from a lack of accuracy and precision and so was not well suited for quantitative analytical work. L'vov did, however, use his device to carry out many studies of the theoretical aspects of atomic absorption.[21] The possibilities for non-flame atomization were largely ignored until the 1969 Atomic Absorption Conference in Sheffield, England, where two new non-flame atomizers were reported. One of these was the carbon filament atomizer developed by T. S. West[22], and the other was the carbon bed atomizer developed by Robinson.[23] Recently, Massman[24] and others have reported modifications of the L'vov device and subsequent work has resulted in a great proliferation of nonflame devices for atomization in atomic absorption spectroscopy.[25, 26, 27] These devices, although very different at first glance, all had several features in common. Invariably, they depended upon the imposition of a sudden pulse of low-voltage, high-amperage electric current through a resistance element. Such a current pulse caused the resistance element to rapidly attain a temperature sufficiently high to cause the thermal decomposition into free atoms of any samples placed on the resistance element. The resistance elements of these atomizers were "sheathed" in a flow of inert gas to avoid oxidation reactions. Devices of this type which depend on thermal decomposition will be referred to hereafter as "electro-thermal" atomizers.

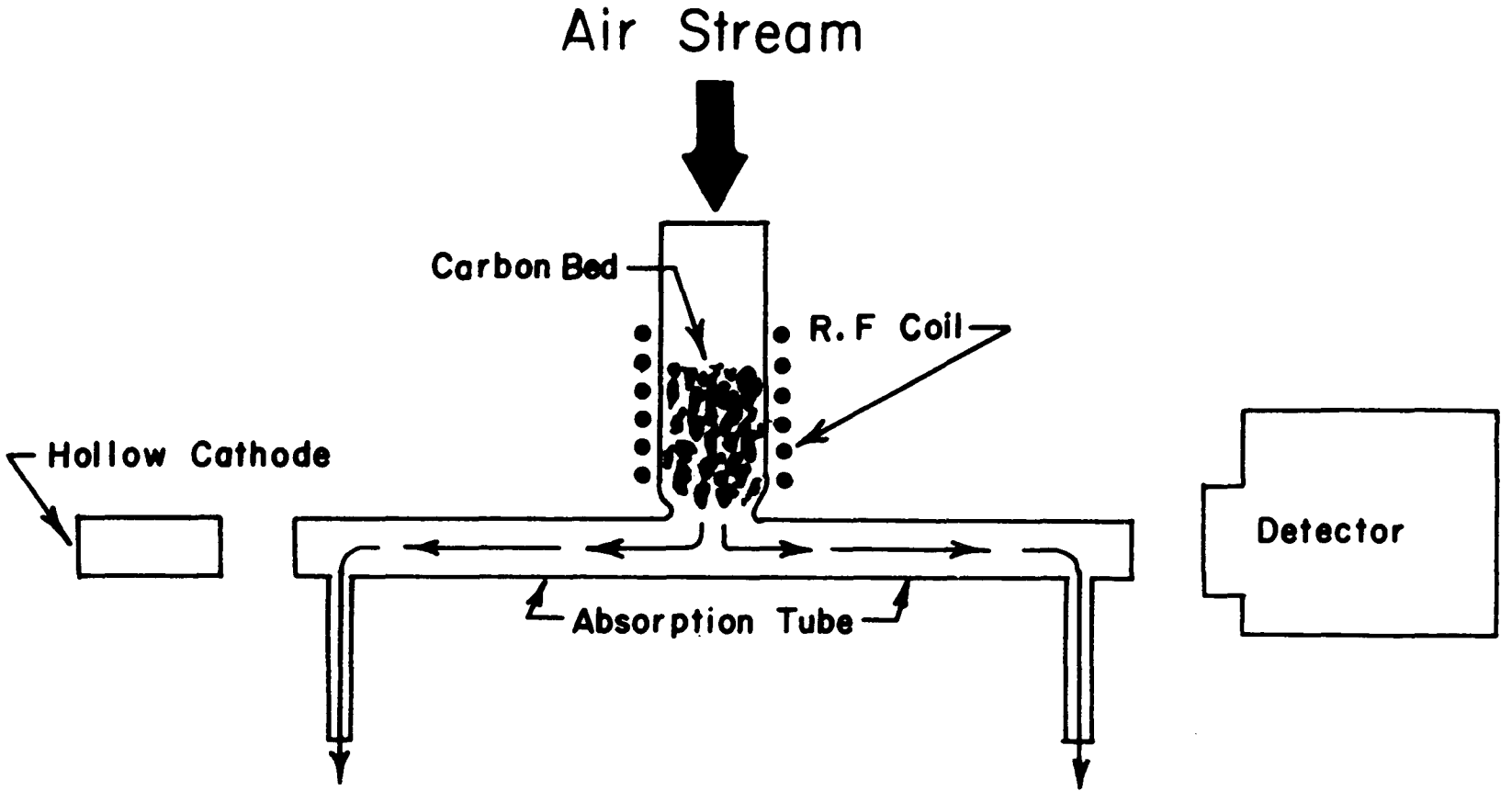
The Robinson carbon bed atomizer, which was initially devised as a means of directly measuring metals in air, was quite different from the various electro-thermal devices previously mentioned. This system, which had been used for the direct determination of lead [28], cadmium[29], and mercury[30,31] in the atmosphere, was the original system from which the atomizer used for this work was derived. Hence, it will be described in some detail. The basic device, shown in Figure 1, consisted of a fused silica "T" cell. The cross-bar of the "T" comprised the optical path of the cell and was sealed at the ends by optical quartz flats, and was maintained at 900-1000° Centigrade by means of resistance heaters. The stem of the "T" contained the atomizer, which consisted of a bed of spectroscopically pure carbon rods maintained at approximately 1250° Centigrade by a radiofrequency induction furnace. To facilitate loading of the carbon rods, and to prevent devitrification of the silica cell, the atomizer bed was placed in a silica liner or "inner sleeve", which slid easily into the stem of the "T". In operation, ambient air was drawn into the stem of the "T" over the carbon rods, where the following reactions occurred:

$$C + O_2 \rightleftharpoons CO \rightleftharpoons CO_2 \qquad 1)$$

$$C + N_2 \rightarrow \text{No reaction} \qquad 2)$$

The $CO \rightleftharpoons CO_2$ equilibrium reaction was displaced entirely in favor of carbon monoxide at temperatures above 900° Centigrade.[32] The sequence of reactions resulted in the removal of all atmospheric oxygen and

Figure 1: Schematic Diagram of the Original Carbon Bed Atomizer



the formation of a highly reducing carbon monoxide atmosphere. Any metallic species contained in the air drawn through the atomizer could react by one or more of three mechanisms to produce free atoms:

$$MX \longrightarrow M^{o} + X^{o} \qquad 3)$$

$$MX + C \longrightarrow M^{o} + C_{m}X_{n} \qquad 4)$$

$$MX + CO \longrightarrow M^{o} + CXO \qquad 5)$$

It was thus easily seen that the efficiency of production of free atoms should be greatly enhanced. The free atoms, once formed, flowed from the atomizer side-stem into the cross-bar of the "T" cell, through which radiation from a hollow cathode was focussed. The decrease in hollow cathode radiation reaching the detector related to the number of free atoms and hence to the analysis of the sample.

This dissertation will describe certain refinements in the original instrument which resulted in increased sensitivity and ease of operation, and overcame some shortcomings in the original design.

In the original work done on the instrument, lead and mercury were investigated.[33] The instrument was calibrated for these elements by techniques involving diffusion or permeation of gaseous species and gas dilution. These techniques were of limited applicability, and so much work was done to design and operate a system which would allow calibration of any metal without the difficulties involved in vapor diffusion. This dissertation will describe the operation of several calibration systems, one of which seems to satisfy particularly the requirements for air pollution calibration.

One of the modifications to the original absorption cell involved the rotation of the atomizer side-stem of the "T" cell from its original horizontal position through an angle of 90^{o} to a vertical position. Such modification resulted in an increased ease by which liquid and solid samples could be introduced into the atomizer. The results of studies into the analysis of solid and liquid samples and the associated problem of molecular background absorption and sample losses will be described and their implications to future applications discussed.

II. EQUIPMENT

A. Atomic Absorption Spectrophotometer :

The atomic absorption spectrophotometer was basically a single-beam spectrophotometric system, using a grating monochromator and a demountable hollow cathode light source. The hollow cathode was replaced by a deuterium discharge lamp for molecular absorption studies. The heart of the device was the unique carbon atomizer-absorption cell combination, which is described in greater detail later in the Equipment section. The carbon atomizer was heated by a radiofrequency induction furnace. For air analysis, an integral part of the system was an air purification network. The complete instrument is depicted schematically in Figure 2 and the instrumental components are listed. The specifications of the individual components are given in the next Section.

B. Instrument Components and Specifications:

a. Monochromator- Jarrel-Ash Model 82-100: 0.5 meter Ebert scanning monochromator with variable slits.

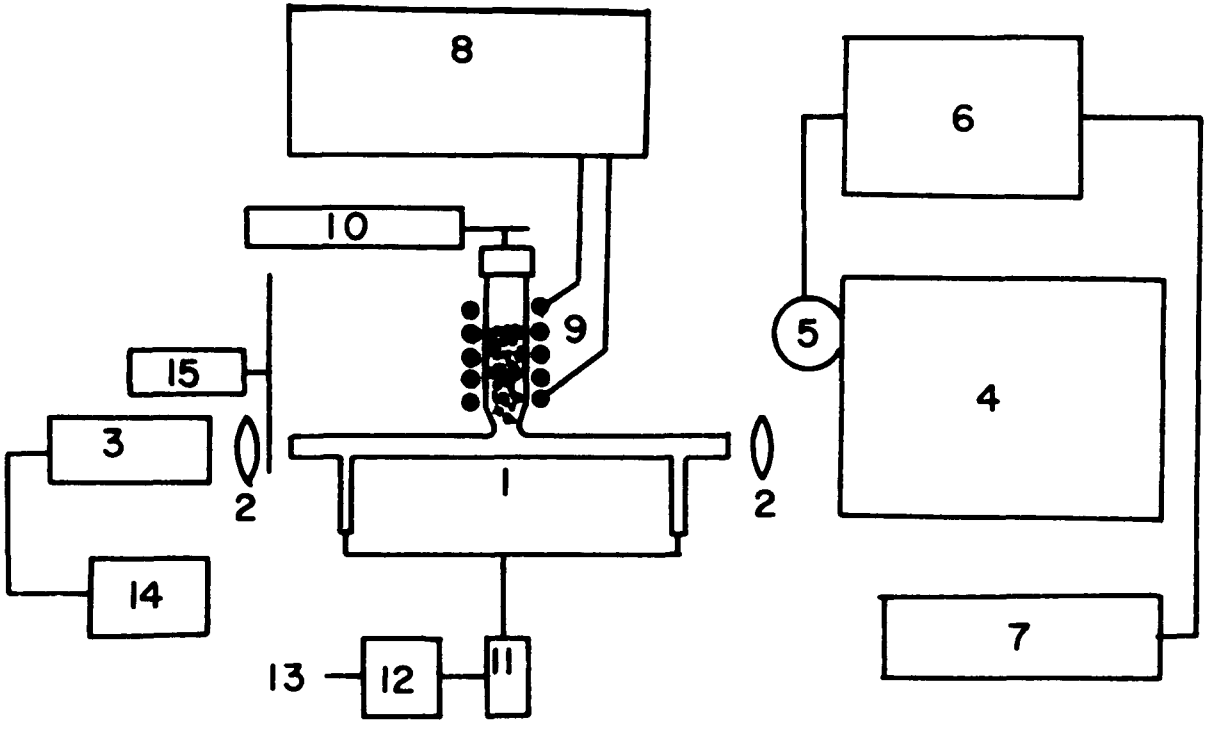
b. Light Sources-
   i. Atomic-Barnes "Glomax" Demountable Hollow Cathode Lamp
   ii. Continuum Source-Beckman Deuterium Lamp Model 96280

c. Detector- Photomultiplier, Model R-106

d. Power Supplies-
   i. Barnes GPS-1 High Voltage Power Supply
   ii. Beckman Deuterium Lamp Power Supply

e. Amplifier- Jarrel-Ash combination broadband AC amplifier-photomultiplier high voltage power supply.

Figure 2: Schematic Diagram and List of Components of the Instrument



1. Absorption Cell
2. Lenses
3. Hollow Cathode
4. Monochromator
5. Photomultiplier
6. Amplifier - High Voltage Power Supply
7. Recorder
8. R.F. Generator
9. R.F. Coil
10. Clean Air Supply
11. Flowmeter
12. Exhaust Pump
13. Exhaust
14. Hollow Cathode Power Supply
15. Chopper

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f. Readout- potentiometric strip-chart recorder, 10-inch, Beckman Model 10005

g. Radiofrequency generator- Lepel 5000 watt, 100 kiloherz induction furnace

h. Chopper- modified stirring motor

i. Optics- Amersil Corporation Suprasil Grade fused silica with 180.0 nm. transmission cutoff.

C. Other Equipment:

a. Vacuum pump-Welch Duo-Seal, Model No. 1404

b. Flow pump-Bantam Vacuum-Pressure Pump Model No. 2064

c. Flowmeter- Matheson Model No. 7228, with Series 620 flow tube.

d. Hamilton syringe- 10 microliter, Model No. 701-N

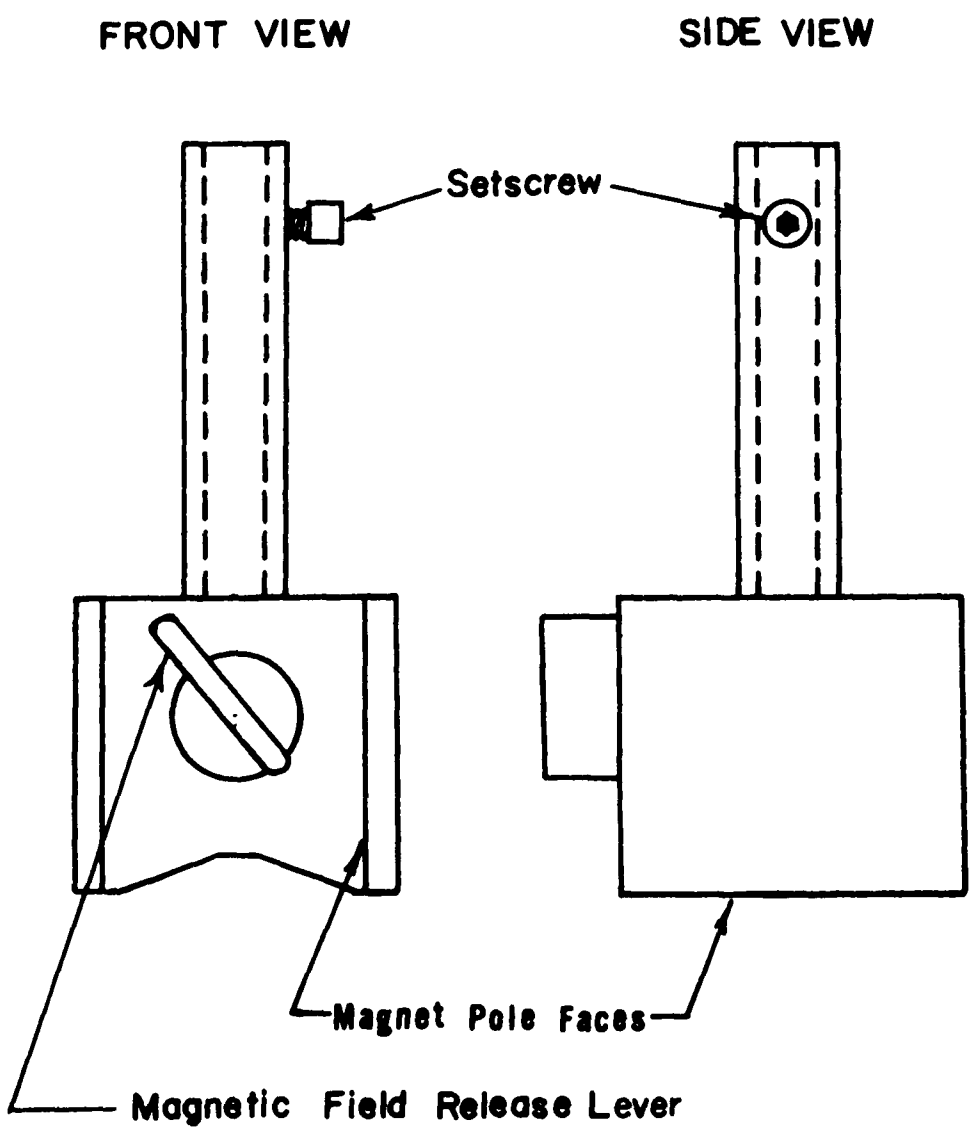
e. Micropipette- Drummond Scientific Microdispenser, 1-5 microliter capacity.

f. Optical Pyrometer- Leeds and Northrup Model No. 750 to 3500 degree centigrade range.

D. Specially Constructed Equipment:

1. Optical table and stands- In order to arrange conveniently the various components of the atomic absorption spectrophotometer, without the limitations imposed by an optical rail, an optical system similar to that described by Winefordner, et al,[34] was constructed. A one half inch thick steel plate was affixed to a table top to provide the optical working area. To hold the spectrophotometer components in position, they were equipped with magnetic bases. The magnetic bases were made by modification of a magnetic scriber mount (National Camera No. 5-716U). The modification involved removing the solid steel support rod with which the mounts were

Figure 3: Modified Magnetic Mounts used as Optical Stands



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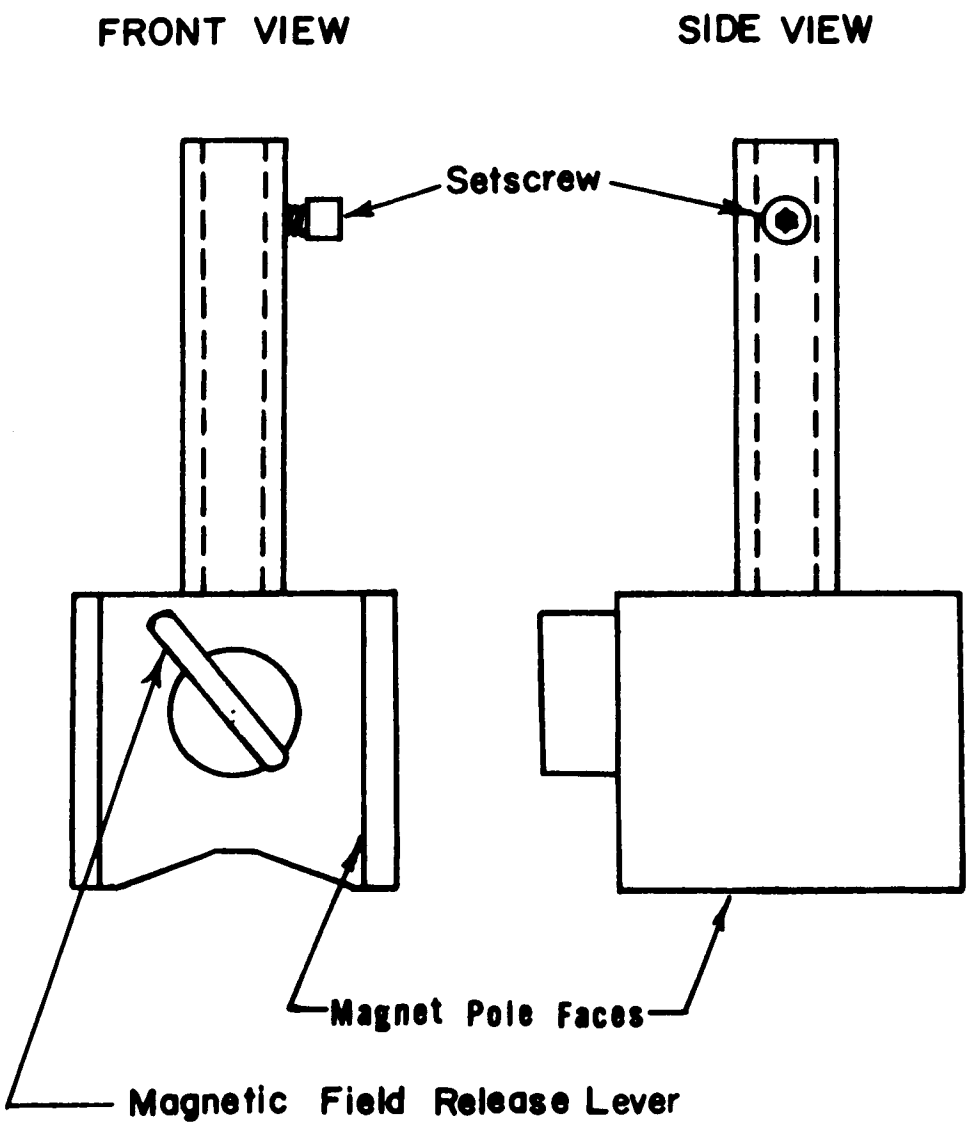
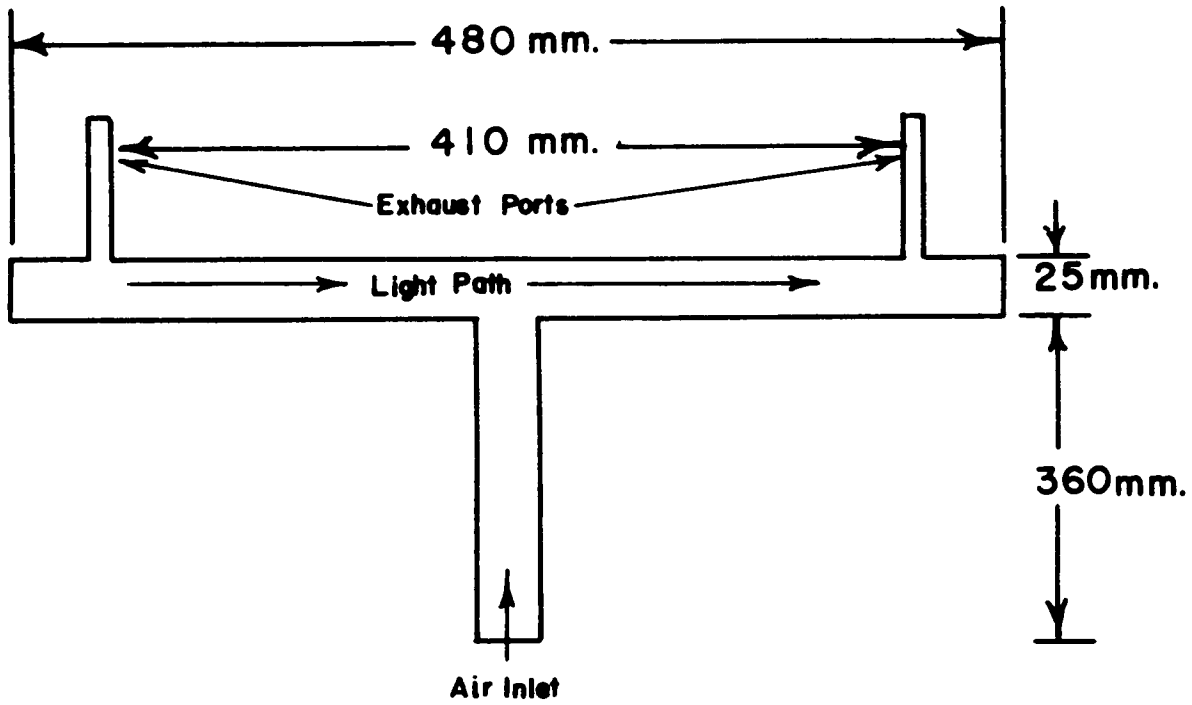


originally equipped, and replacing them with four-inch long hollow brass rods and setscrews. The modified base is shown in Figure 3. Since these magnetic bases were designed to allow the magnetic clamping action to be turned "on" or "off", the various components could be easily shifted into any position and rigidly clamped into place. Such a system offered maximum versatility in arranging and moving the components of the spectrophotometer.

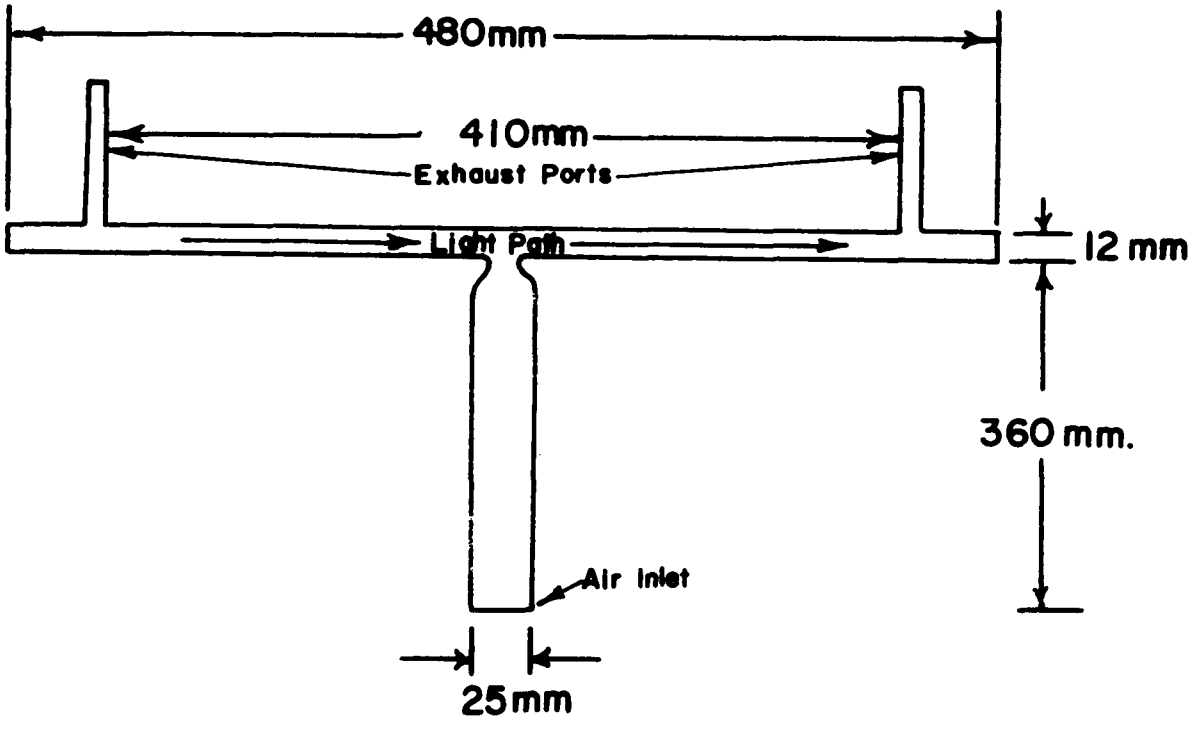
2. Absorption Cell: The absorption cells used in this work were similar to those used by previous workers in this research group.[35] The original absorption cell was constructed of fused silica in the shape of a "T". A diagram of the original absorption cell is shown in Figure 4. As mentioned previously, the cross-bar of the "T" was the light-path of the absorption cell, and the stem of the "T" contained the atomizer. The original workers found that placing the atomizer carbon in direct contact with the silica of the atomizer stem of the absorption cell caused devitrification of the silica and breakage of the cell. To avoid having to replace the "T" types, inner sleeve linings of silica were placed inside the cell stem. These inner sleeves could be easily removed and discarded as they devitrified, thus extending the lifetime of the absorption cell. The original absorption cell was used for work involving air flow rates through the cell of the order of 1200 cm^3/minute. Since the cell volume was approximately 500 cm^3, the time required for a complete turnover of air in the cell was about 30 seconds. Such a length of time resulted in adequate analytical response times when changing from one air sample to another.

Figure 4: Original Absorption Cell used in Early Experimental Work



Original Absorption Cell

Figure 5: Modified Absorption Cell Used in Low Flow Rate Studies

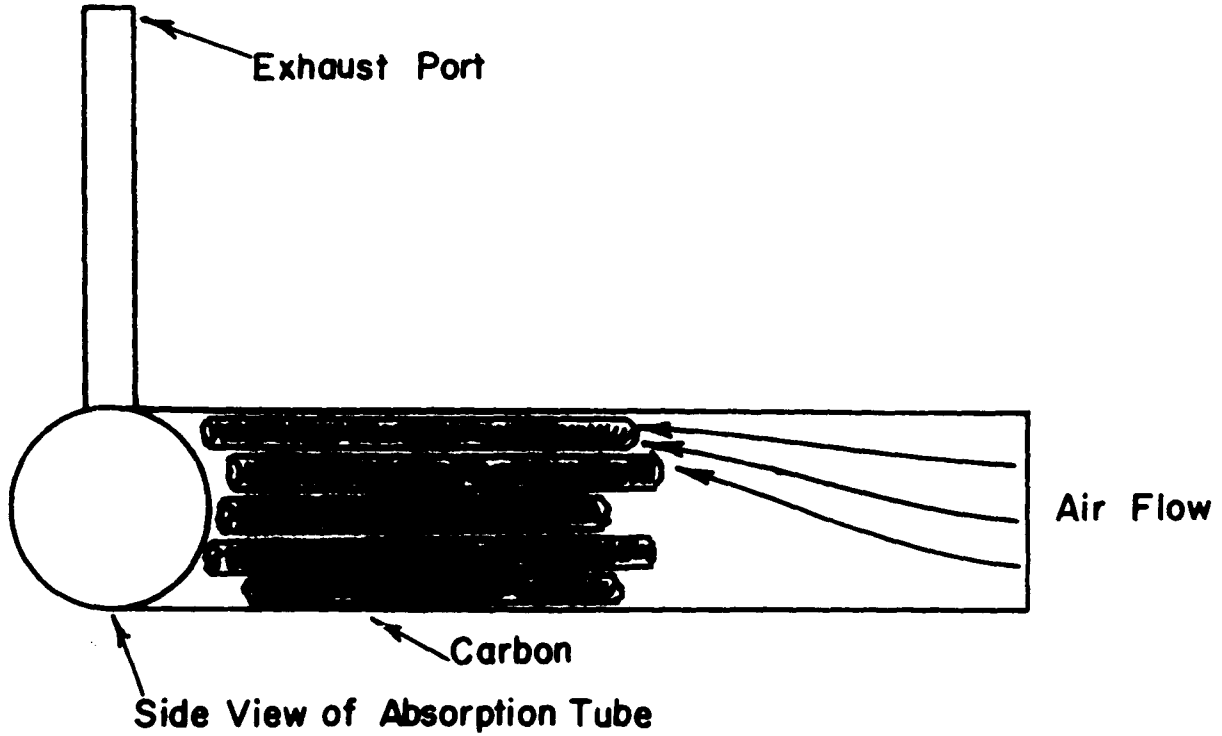


Modified Absorption Cell

It was felt that flow rates lower than 1200 cm^3/minute might result in greater atomization efficiency, hence flow rates of the order of 100 cm^3/minute were tried. At such a low flow rate, five minutes were required for a complete exchange of air through the cell. It was found experimentally that this resulted in an unacceptably slow analytical response time. To overcome the difficulty, the cell shown in Figure 5 was constructed. This cell was reduced in volume to approximately 100 cm^3 by changing the diameter of the light-path from 25 mm. to 12 mm. The change in diameter resulted in increased speed of analytical response without sacrificing any optical path length.

3. Atomizer: A more important modification of the absorption-cell atomizer system was in devising a means of mounting the carbon atomizer "T" stem vertically rather than horizontally, as had been done by previous workers.[36] The factor that necessitated such a design change is shown in Figure 6. In the original horizontally mounted carbon atomizer, the radiant heating of the incoming air by the intensely hot carbon resulted in the establishment of an density gradient and preferential air-flow path. The preferred air-flow path resulted in the combustion of the carbon at the top of the carbon bed and the formation of an open channel through which air flowed. Passage of sample air over the carbon could reduce atomization efficiency by reducing the time the sample would be in contact with the hot carbon atomizer. By-passing the carbon could also result in the incomplete reduction of atmospheric oxygen to

Figure 6: Preferential Flow-path in Horizontally Mounted Absorption Cell



carbon monoxide. It was felt that such a possibility must be avoided, and that mounting the atomizer sidearm vertically would overcome the problem by eliminating the density gradieny with a downward airflow.

In order to accomplish the vertical mounting, two things were necessary: 1) a means to hold the atomizer carbon inside the inner sleeve when the atomizer sidearm was mounted vertically, and 2) some means to prevent the inner sleeve from blocking the light path. The first difficulty was overcome by placing a perforated porcelain disc in the end of the inner sleeve. The porcelain disc fulfilled two highly critical requirements: it was stable in the highly reducing carbon monoxide atmosphere, and it could withstand deterioration from prolonged contact with intensely hot carbon. Originally, an attempt was made to affix the porcelain disc to the end of the inner sleeve with quartz cement. This procedure failed as the cement was not stable at the conditions of temperature and atmosphere in the atomizer. The problem was finally solved by reducing slightly the diameter of one end of the inner sleeve and placing the porcelain disc within the reduced portion. The weight of the carbon atomizer charge then held the disc in place. The final arrangement of the inner sleeve and porcelain disc as used throughout the rest of the work is shown in Figure 7.

The second difficulty mentioned with respect to the vertical mounting of the atomizer sidearm was the necessity to prevent the inner sleeve from blocking the lightpath. This difficulty was overcome by the device shown in Figure 8. This

Figure 7: Support of Atomizer Carbon in Vertical Sidearm

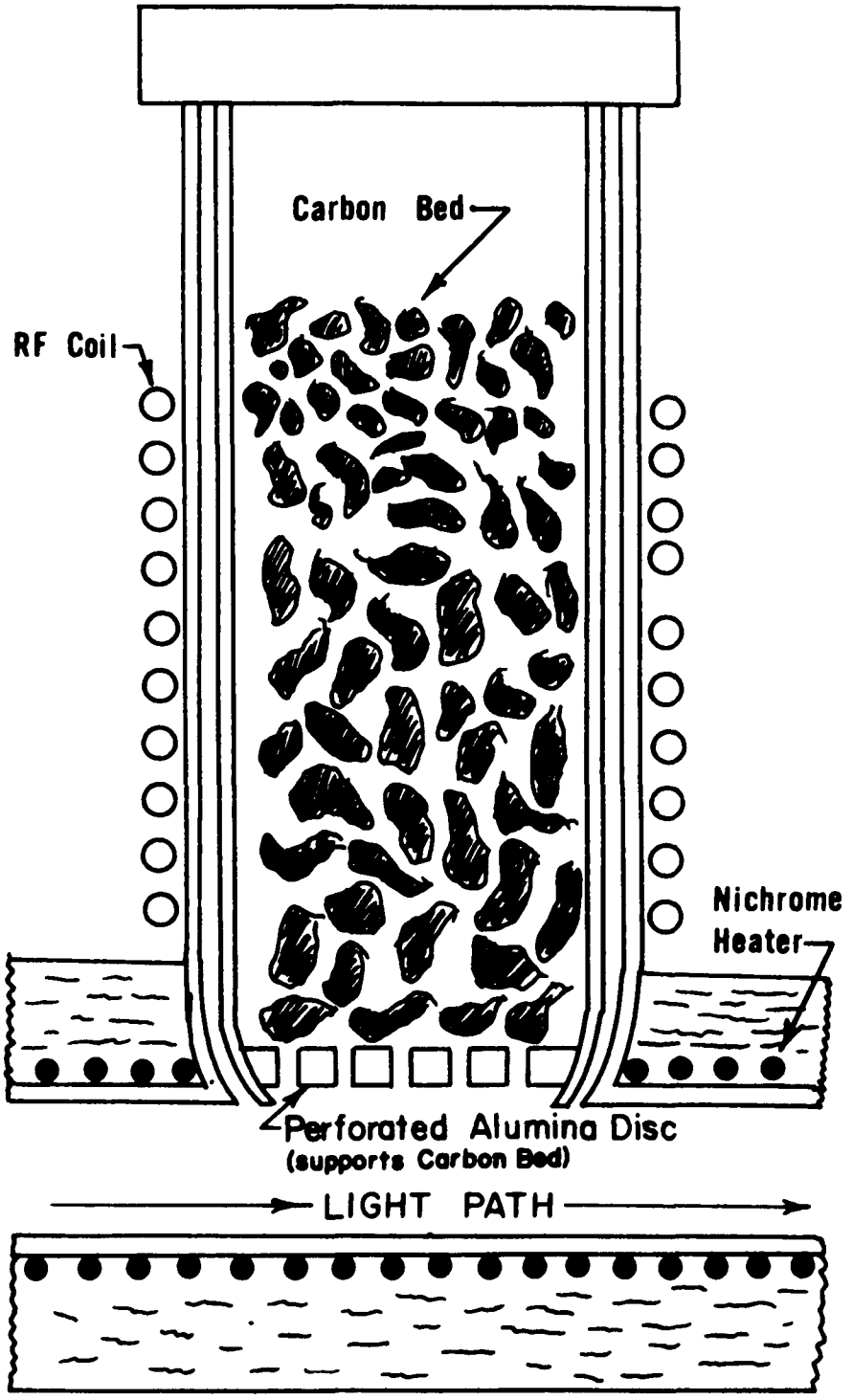


Figure 8: Sleeve Adaptor for Supporting the Inner Sleeve in the Vertical Sidearm

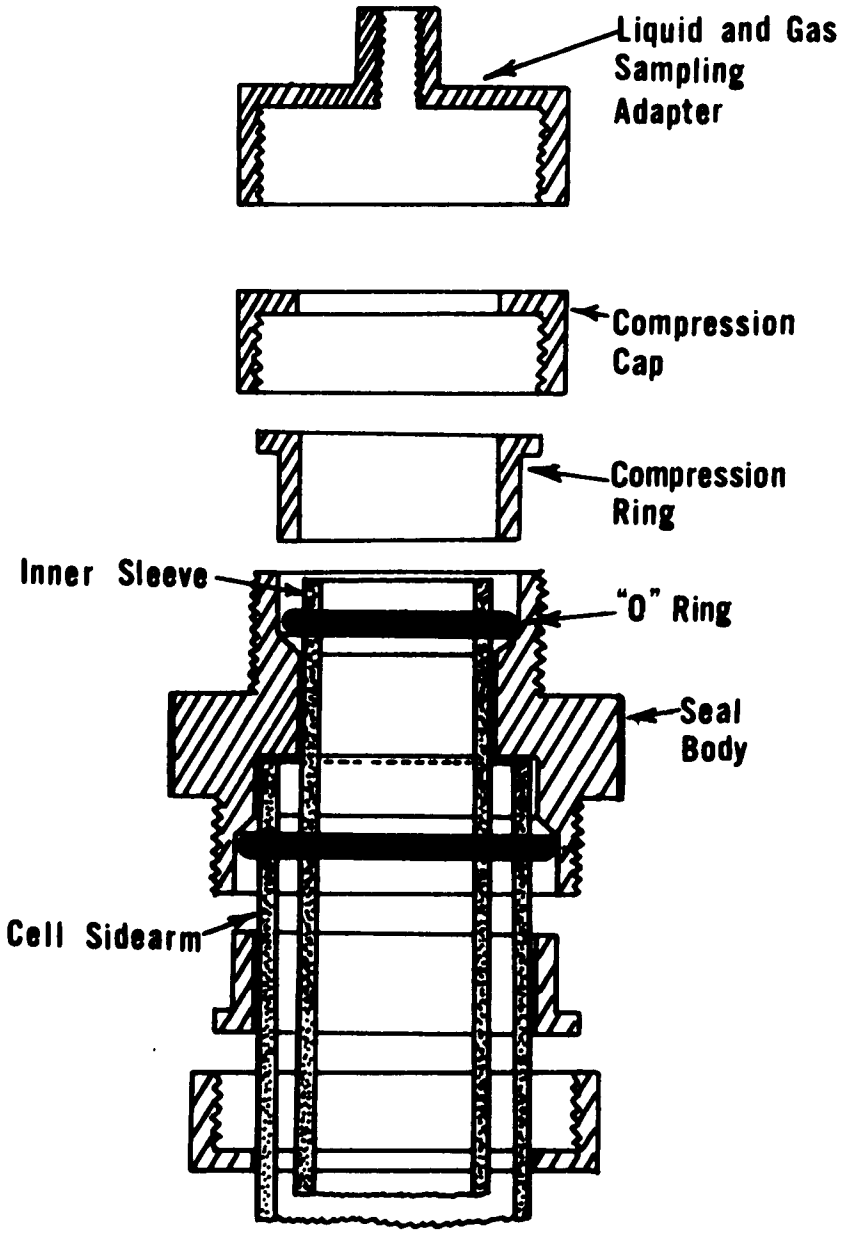
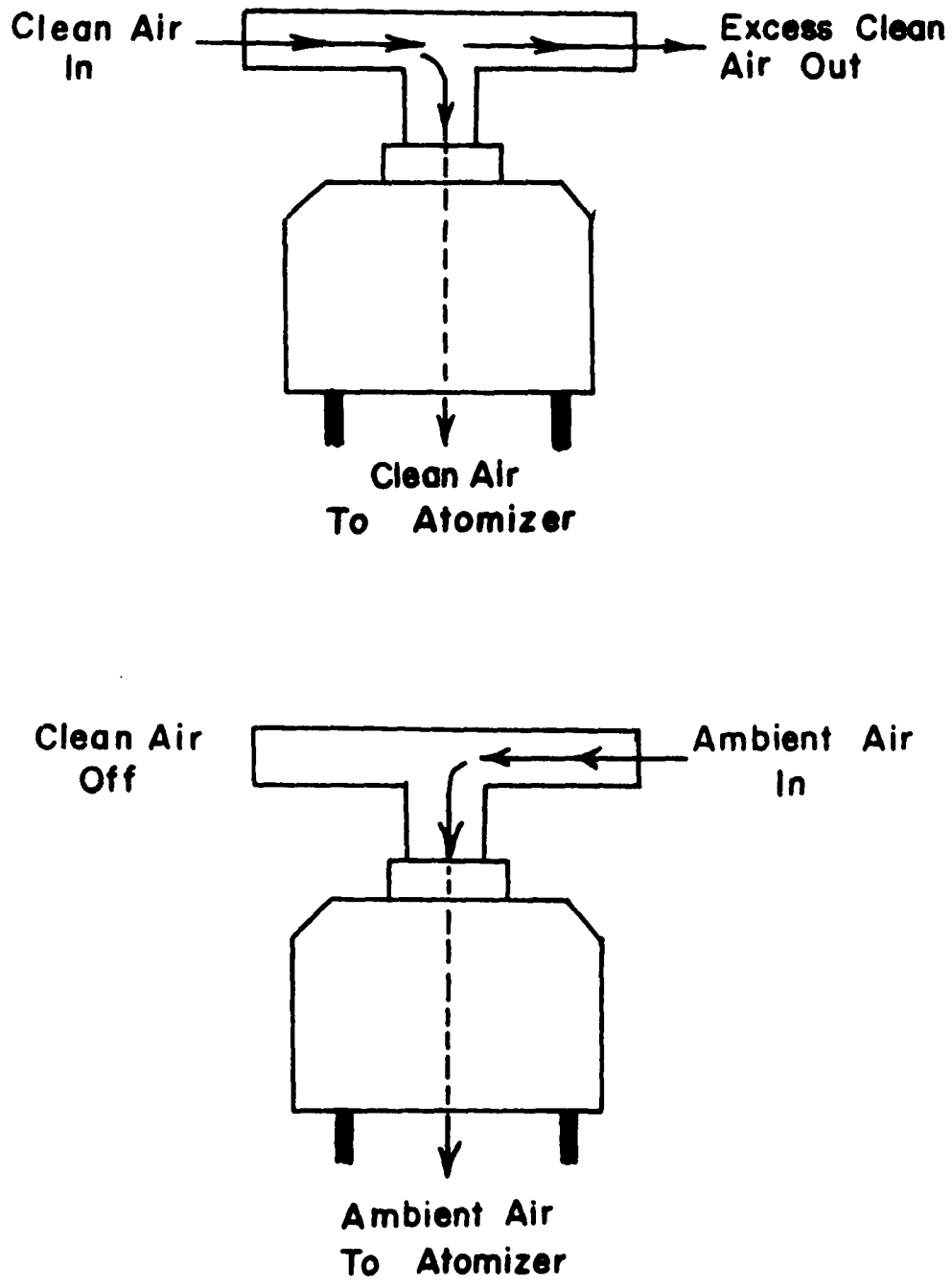


Figure 9: Constant Pressure Sampling Head for the Introduction of Clean Air and Ambient Air Samples



"sleeve adaptor" made it possible to support the inner sleeve in a vertical position. It also provided an airtight, "O" ring seal between the inner sleeve and the sidearm of the absorption cell.

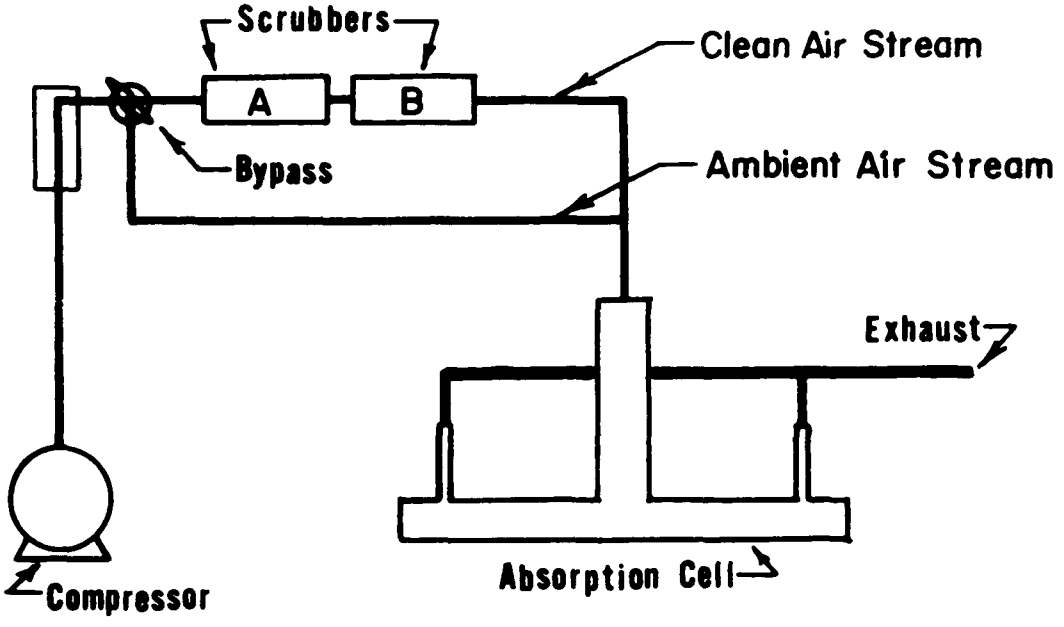
The sampling head of the device, shown in Figure 9, allowed the easy introduction of samples of "ambient" (polluted) or "clean" (scrubbed) air, and convenience in switching from one air-stream to another.

A not unexpected advantage of vertically mounting the atomizer sidearm was the increased ease with which solid and liquid samples could be introduced into the atomizer. This modification made it possible to investigate the feasibility of the direct analysis of liquid and solid samples with the carbon bed atomizer. The results of the investigation with solid and liquid samples are described later.

4. Air Flow System: In order to obtain useful analytical data on metallic pollution of the air, it was necessary to be able to establish a zero baseline for the instrument. This can only be done accurately by analyzing clean air. This necessitated a source of "clean" (metal-free) air. It was also necessary to be able to interchange "clean" and polluted air in order to compare the two. Also required was a system to provide the necessary pressure differential to drive air through the atomizer-absorption cell.

Previous workers in this laboratory have used a system similar to that shown in Figure 10.[36] In the system shown, air flow through the absorption cell was accomplished by means of a pressure differential imposed at the system inlet by a small compressor.

Figure 10: Air-Flow System Using a Compressor



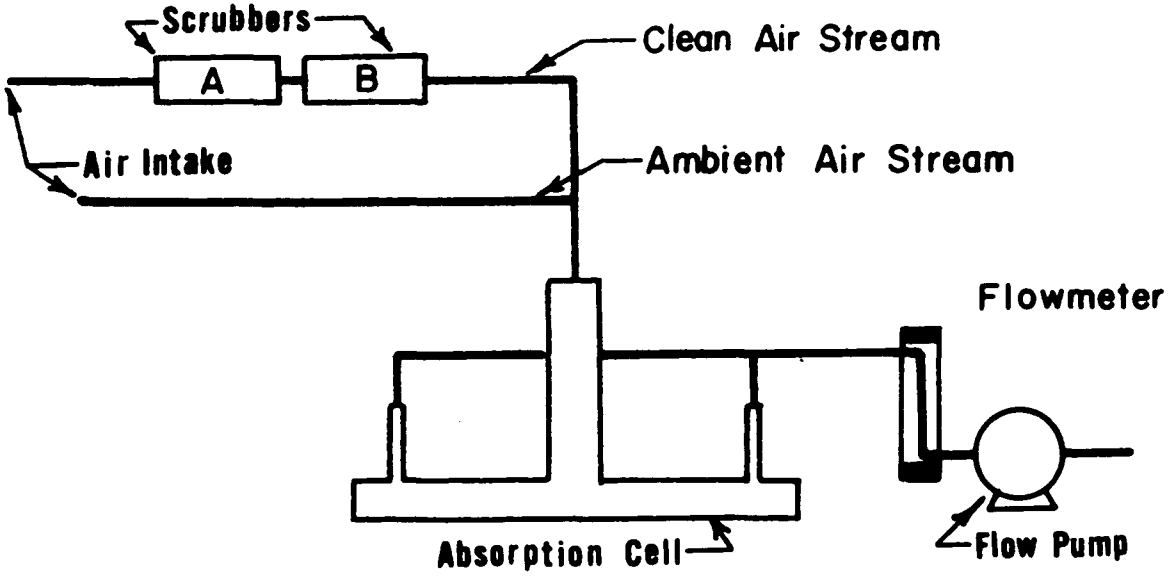
A= Calcium Chloride

B= Activated Charcoal

The compressor was the driving force for air-flow through the cleaning network (to be described later) and through the sampling network. The major disadvantage of this system was the necessity for the ambient air sample to flow through the compressor and associated tubing. Passing the sample air through the compressor could result in sample losses in the compressor of particulate or molecular species of interest. There was also the possibility of introducing contamination from the moving parts of the compressor. With these drawbacks, it was felt necessary to change from a system in which the pressure differential for air-flow was imposed at the system inlet (a "pushing" system), to one in which air-flow was accomplished by a pressure differential imposed at the exhaust (i.e. a "pulling" system). With such a system, the necessity for the sample air to pass through a compressor would be eliminated.

To accomplish the above-stated objective, the system shown in Figure 11 was constructed. In the system depicted, air-flow was attained through both the air-cleaning network and through the sampling network by a small diaphragm vacuum flow pump at the exhaust ports of the atomizer-cell. When sampling ambient air, the sample air flowed through a minimum of tubing and the possibility of sample loss was greatly reduced. Upon actually operating the system it was noted that routing the air-stream through the cleaning network caused a drastic decrease in flow-rates. The drop in flow rate was caused by the increased resistance to flow of the cleaning network as compared to the ambient air inlet. Since it was necessary to maintain atomization conditions as nearly constant as possible, the situation was intolerable.

Figure 11: Air-Flow System Using Vacuum Flow-Pump



A = Calcium Chloride

B = Activated Charcoal

To eliminate the air-flow problems caused by the pressure drop through the scrubbing materials, the system was modified as shown in Figure 12. With this modification, the driving force to attain air-flow through the scrubbing materials was provided by pressurized air from a compressed air tank. The compressed air flowed through the cleaning network and then to the sampling head of the sleeve adaptor, which allowed the pressure to "float" at atmospheric. The vacuum flow pump then "scavenged" clean air from the air-stream at low flow rates, drawing it through the atomizer. In this fashion, fluctuations in flow rate were eliminated.

5. Clean Air System: As had been mentioned earlier, it was necessary to provide a sample of air which was free of molecular and particulate contaminants to form a reference to which pollution levels could be compared. A system for removing contaminants from air streams is shown in Figure 13. The system consisted of: a) compressed air source, b) drying column (calcium chloride), c) activated charcoal adsorption column, and d) Millipore filter (0.45 micron pore size). This system was used throughout the work and was found to be quite effective in removing contaminants from the air-stream.

6. Platinum Loop Liquid Injector- A system for introducing liquid samples into the atomizer as vapors is shown in Figure 14. The device consisted of a small loop of 24 gauge platinum wire connected to two stainless steel electrodes by means of small set-screws. The stainless steel electrodes were connected to the secondary windings of a 6.3 volt filament transformer. The primary

Figure 12: Air-Flow System Modified to Avoid Pressure Fluctuations

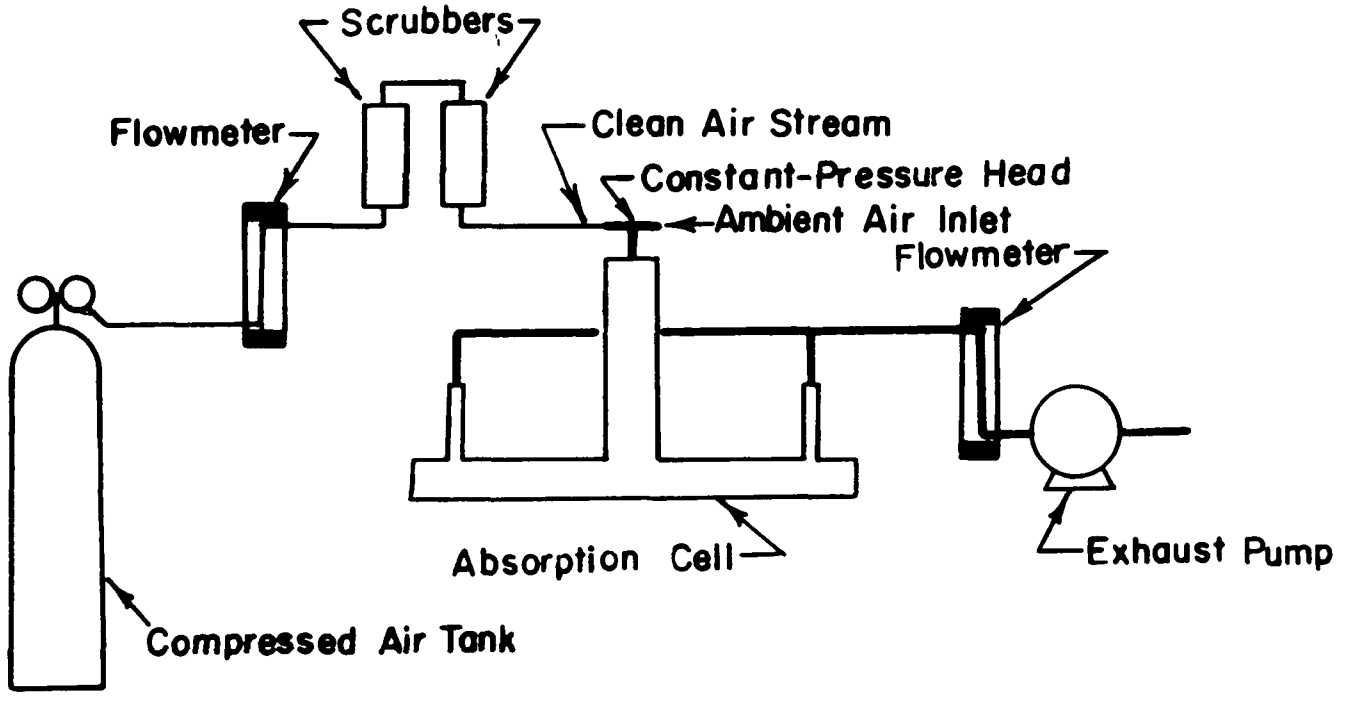
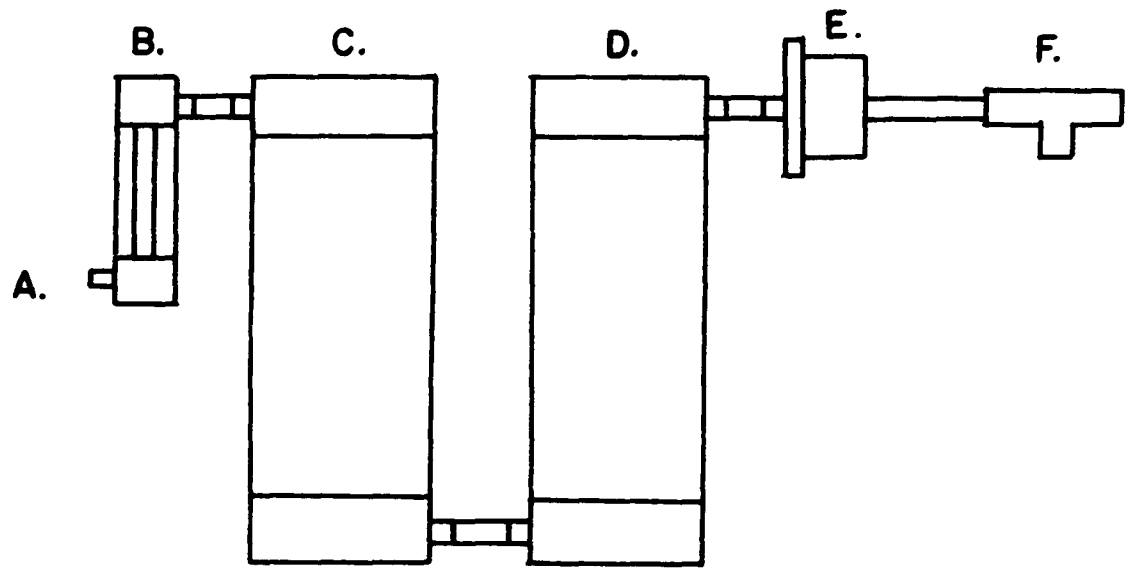


Figure 13: Air Purification System For Removal of Metallic Contaminants



A. Air Inlet
B. Flowmeter
C. Calcium Chloride Drying Column
D. Activated Charcoal
E. Millipore Filter
F. Constant Pressure Head

Figure 14: Schematic Diagram of Platinum Loop Injector for Introduction of Liquid Samples

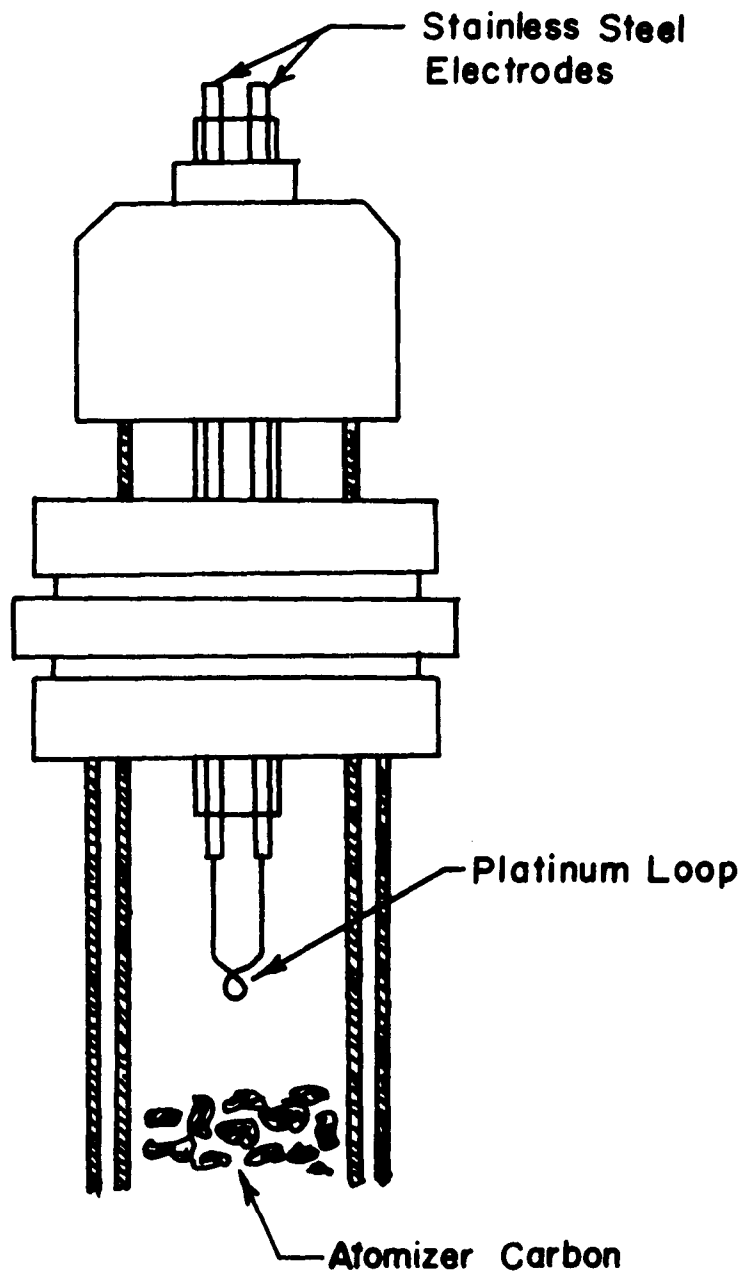
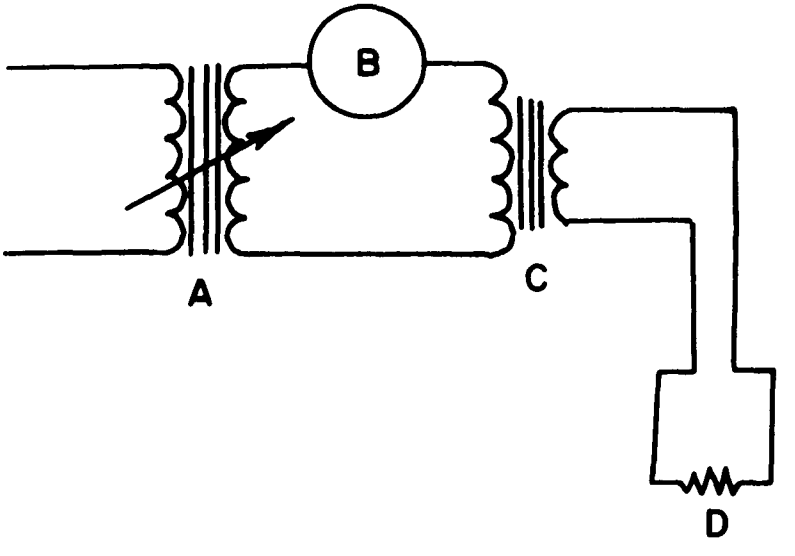


Figure 15: Circuit Diagram of Platinum Loop Liquid Injector



A. Variable Transformer

B. Ammeter

C. Filament Transformer

D. Platinum Loop

winding of the filament transformer was connected to a 0-140 volt variable transformer (Variac). At full power, the system was capable of heating the platinum wire to its melting point in approximately two seconds. The circuit diagram of the injector is shown in Figure 15.

7. Direct Drop Liquid Injector: Another system for introducing liquid samples onto the atomizer bed is shown in Figure 16. In this system the sampling head held a Hamilton syringe, which was used to inject liquid drops directly onto the hot carbon. The sampling head used for direct drop injection was of slightly different configuration from that used originally for air sampling, but it retained the advantage of allowing the clean air source to "float" at atmospheric pressure while injecting liquids under clean air conditions.

8. Hamilton Syringe Modification: The Hamilton syringe, as originally furnished, employed a standard septum penetrating needle, shown in Figure 17a. It was found that this needle point possessed too much surface area for the surface tension to allow liquid drops to fall off. To reduce the surface area, the needle was machined to a pipette point, as shown in Figure 17b. Such modification resulted in a lowering of surface area and greater ease of droplet injection. Hamilton syringes with pipette points could be obtained commercially.

9. Micropipette Modification: It was found that the Hamilton syringe was limited in its ability to deliver a sample drop reproducibly onto the carbon bed. It was felt that such limitation was due to the large dead volume of the needle, and that the precision could be improved if the dead volume could be eliminated.

Figure 16: Direct Drop Liquid Injector for Introduction of Liquid Samples

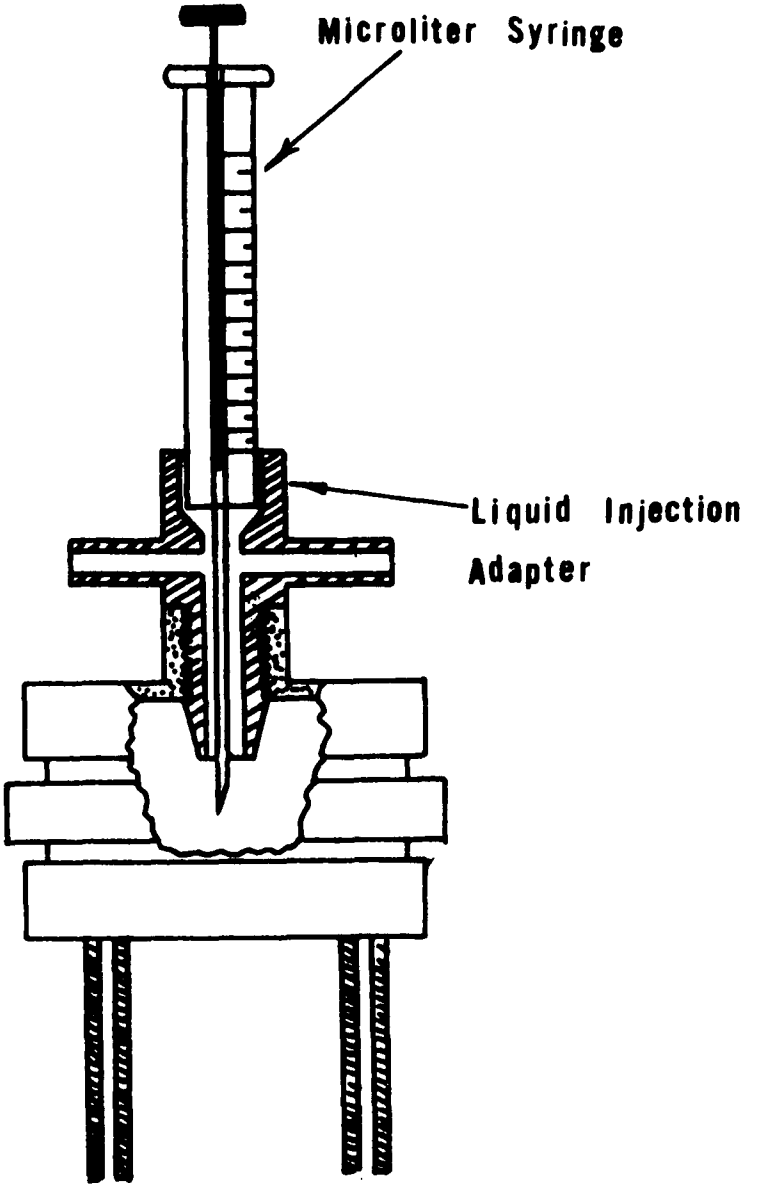
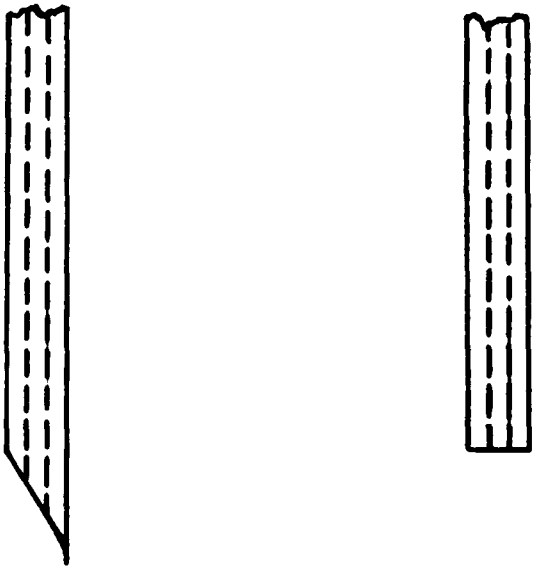


Figure 17: Modification of Hamilton Syringe Needle from Septum Point to Pipette Point

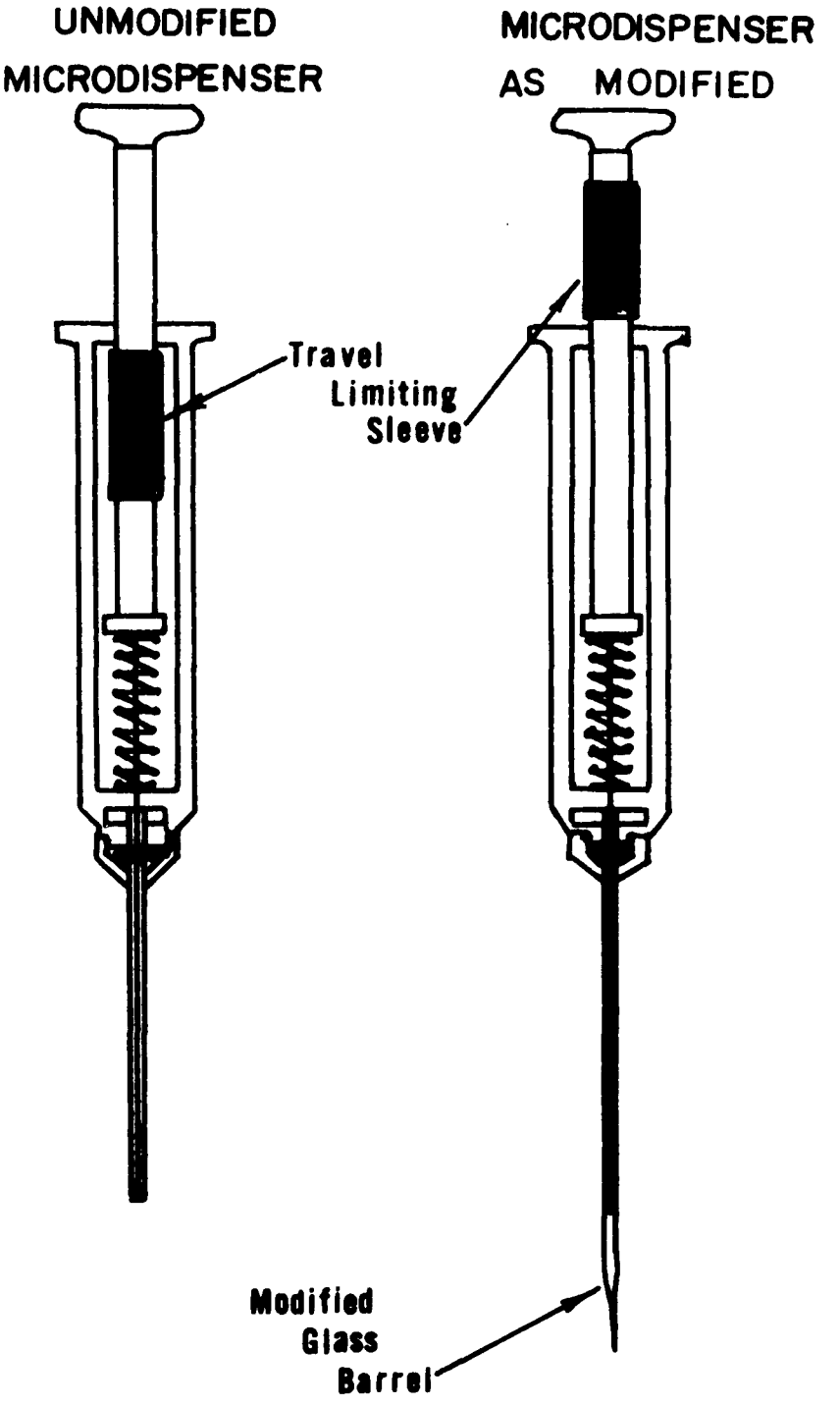


Septum Point

Pipette Point

It was decided to obtain a pipetting device with a plunger which travelled the entire length of the needle. Such a device was the Drummond Scientific Corporation's Microdispenser, which employed a disposable glass barrel. The plunger of the Microdispenser traversed the entire length of the barrel. As delivered, the syringe was unsatisfactory, due to excessive drop hangup. The original Microdispenser is shown in Figure 18a. By drawing a fine capillary tip on the end of the glass barrel, and transferring the travel limiting sleeve from inside the pipette body to the plunger, as shown in Figure 18b, the microdispenser was converted to an air-displacement device. In the modified device, an excess volume of air was retained between the plunger and the sample. Upon pressing the plunger, the excess air assured that the entire volume of liquid was ejected from the barrel.

Figure 18: Drummond Microdispenser Modified for Air-Displacement Liquid Injection



III. EXPERIMENTAL AND RESULTS

A. Factors Affecting Atomization and Atomic Absorption Signal

1. Introduction: In operation, the Robinson carbon bed atomizer was similar to other atomic absorption techniques, except in the method of generating and maintaining the population of free atoms. As has been discussed previously, the atomizer consisted of a bed of carbon pieces, maintained at 1300-1500° Centigrade by means of a radiofrequency induction furnace. Upon contact with the hot carbon, atmospheric oxygen reacted with the hot carbon to produce carbon monoxide, which provided an excellent set of conditions for the formation of free atoms. Metallic species could be reduced to the free atomic state by three mechanisms: a) thermal decomposition, b) chemical reduction by carbon, and c) chemical reduction by carbon monoxide. It was apparent that the efficiency of formation of free atoms was affected by any factor which influenced these three methods of reduction.

The first factor considered was temperature. Obviously, the thermal decomposition of metallic species must be important in the formation of free atoms; indeed, for the electrothermal atomizers, it was the only means of atomization. In the carbon bed atomizer, the temperature was related to the radiofrequency power that could be coupled with the carbon pieces. The carbon pieces constituted the atomizer "charge." In the terminology of induction heating, the object or collection of objects heated by the radiofrequency field was called the "charge" of the induction furnace.

The theory of radiofrequency induction heating showed that the quantity of energy that can be coupled with the charge was influenced by several factors. These factors were: a) the total size (weight) of the charge, b) the geometrical shape of the charge (or of the individual pieces if the charge was made up of more than one object), c) the position of the charge within the radiofrequency field, and d) the frequency of the radiofrequency generator.[37]

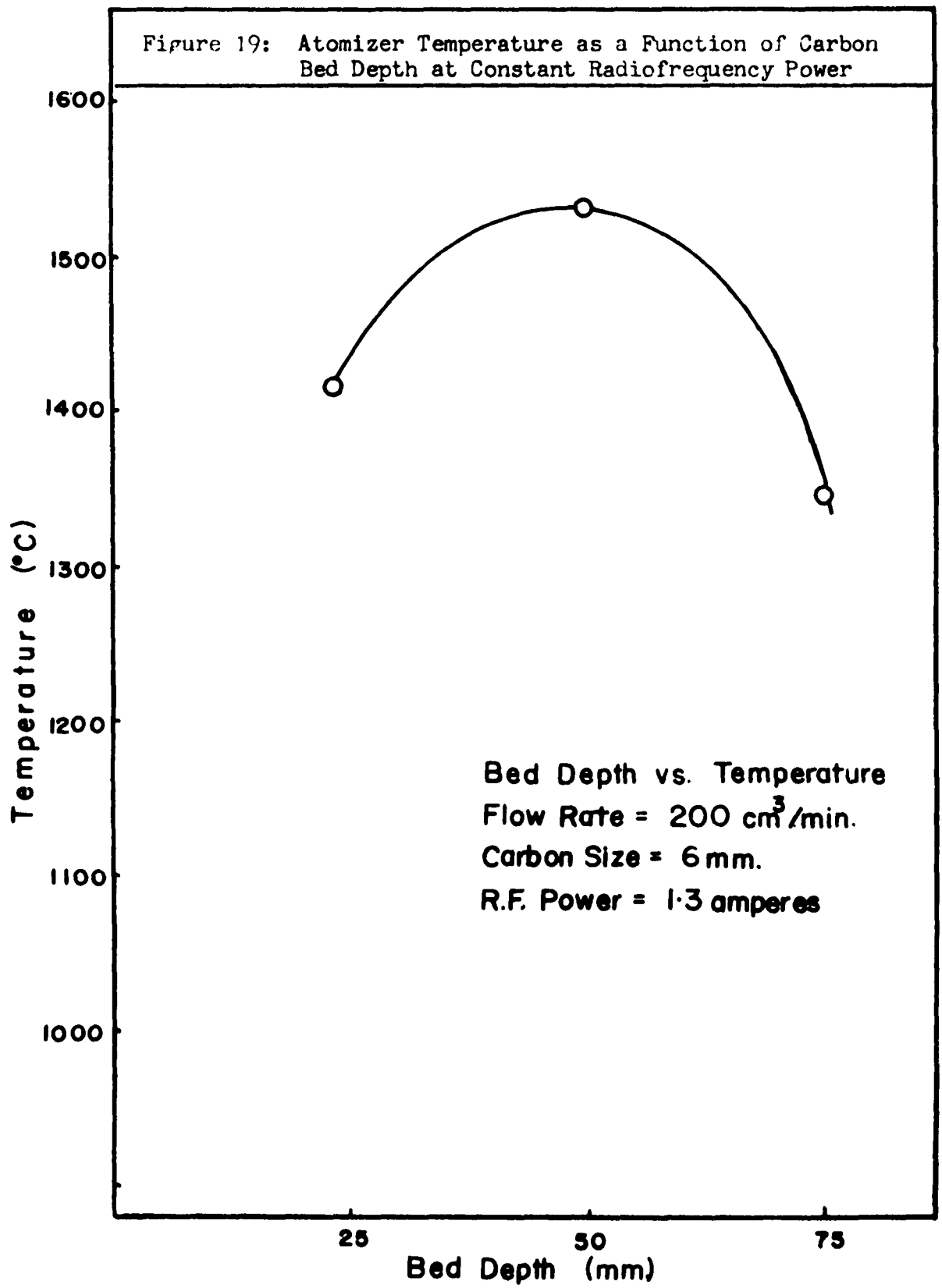
Since the amount of energy coupled into the charge depended upon these factors, the temperature also depended upon them. Consequently, an investigation into these factors and their effect upon atomizer temperature was undertaken.

The other factor of importance in determining the atomization efficiency was the flow rate of air through the carbon bed. This factor governed the length of time any sample species spent in the atomizer, and thus its chances of being reduced to the free atomic state.

2. Experimental and Discussion:

a. Factors Affecting Temperature: The first factor investigated was the effect of charge size (total weight of atomizer carbon) upon temperature. The experiment was carried out by placing different amounts of carbon in the atomizer, and measuring the temperature of each different size charge at constant frequency and plate current. The data obtained were expressed as temperature as a function of depth of the carbon bed, and were plotted in Figure 19. These data indicated that maximum coupling efficiency occurred at a bed depth of 50 mm. The data were confusing at first glance, since

Figure 19: Atomizer Temperature as a Function of Carbon Bed Depth at Constant Radiofrequency Power



if the entire amount of energy was being coupled into the charge, maximum temperature should have been attained for the 25 mm. deep carbon bed. If the position of the charge in the induction coil was also taken into consideration, the data were easily explained:

a) The 25 mm. bed was located at the bottom of the radiofrequency coil in an area in which the electromagnetic field was diverging. Hence the power of the radiofrequency field was not effectively coupled into the carbon.

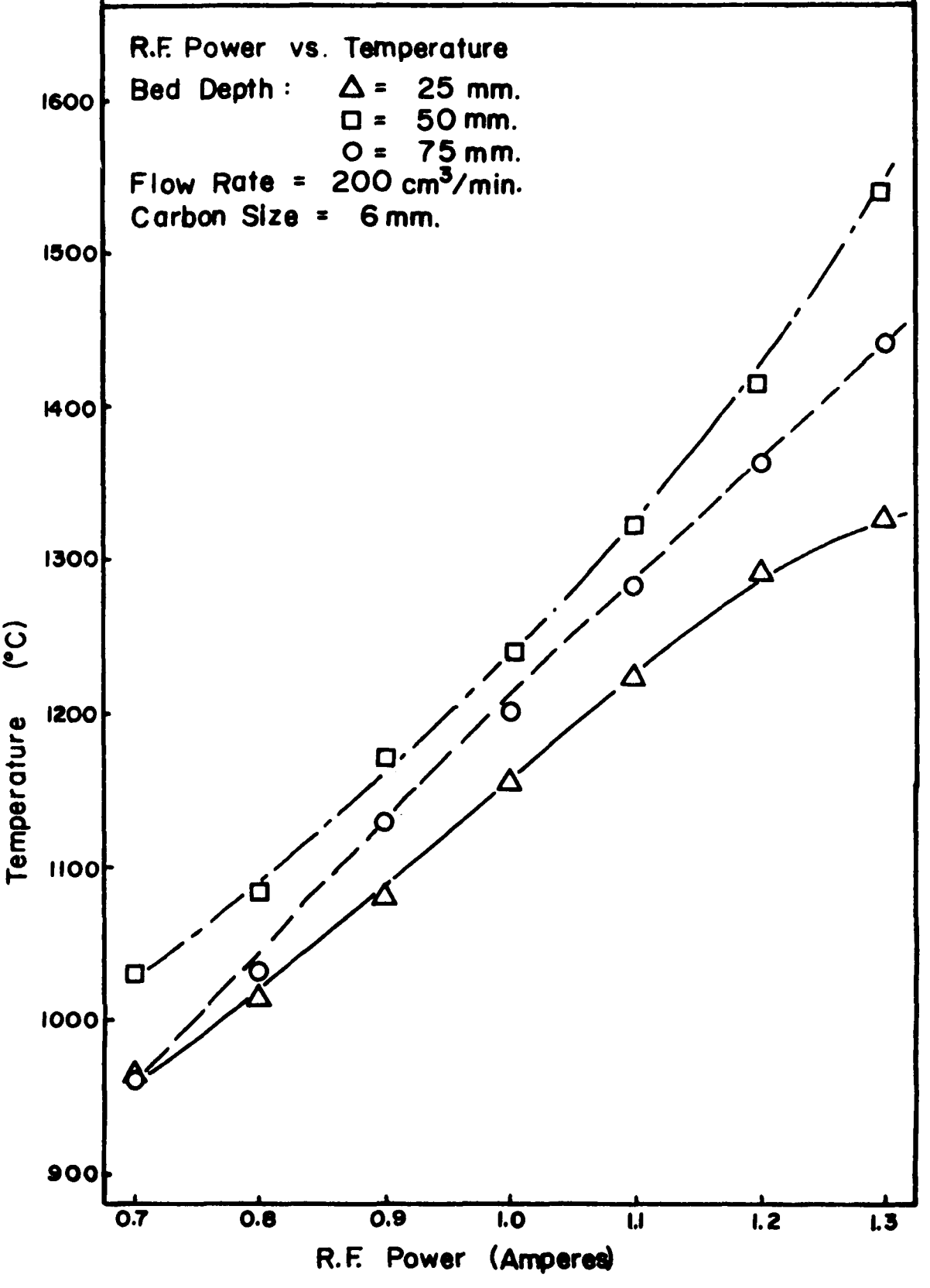
b) The largest portion of the 50 mm. deep bed was located in the center of the radiofrequency coil, in the region of maximum coupling efficiency. The lower 25 mm. of the bed was maintained at the higher temperature by conduction and convection from the hotter portion of the bed.

c) The 75 mm. deep bed had coupled the same amount of radiofrequency power as the 50 mm. bed, but the quantity of carbon to be heated was one-third greater. Hence the energy density in the individual carbon pieces of the atomizer charge was lower, and the temperature was reduced.

The plate current of the radiofrequency generator was an indication of the amount of energy coupled into the atomizer charge and thus had a direct effect upon temperature. This effect was determined for each of the different depths of carbon beds. The data are plotted in Figure 20.

The curves indicated that the efficiency of coupling decreased with increasing plate current for the 25 mm. deep carbon bed. This effect was indicated by the decrease in slope of the curve for high values of plate current. This data indicated that

Figure 20: Atomizer Temperature as a Function of Plate Current at Constant Frequency



the maximum amount of energy possible was coupled into the carbon.

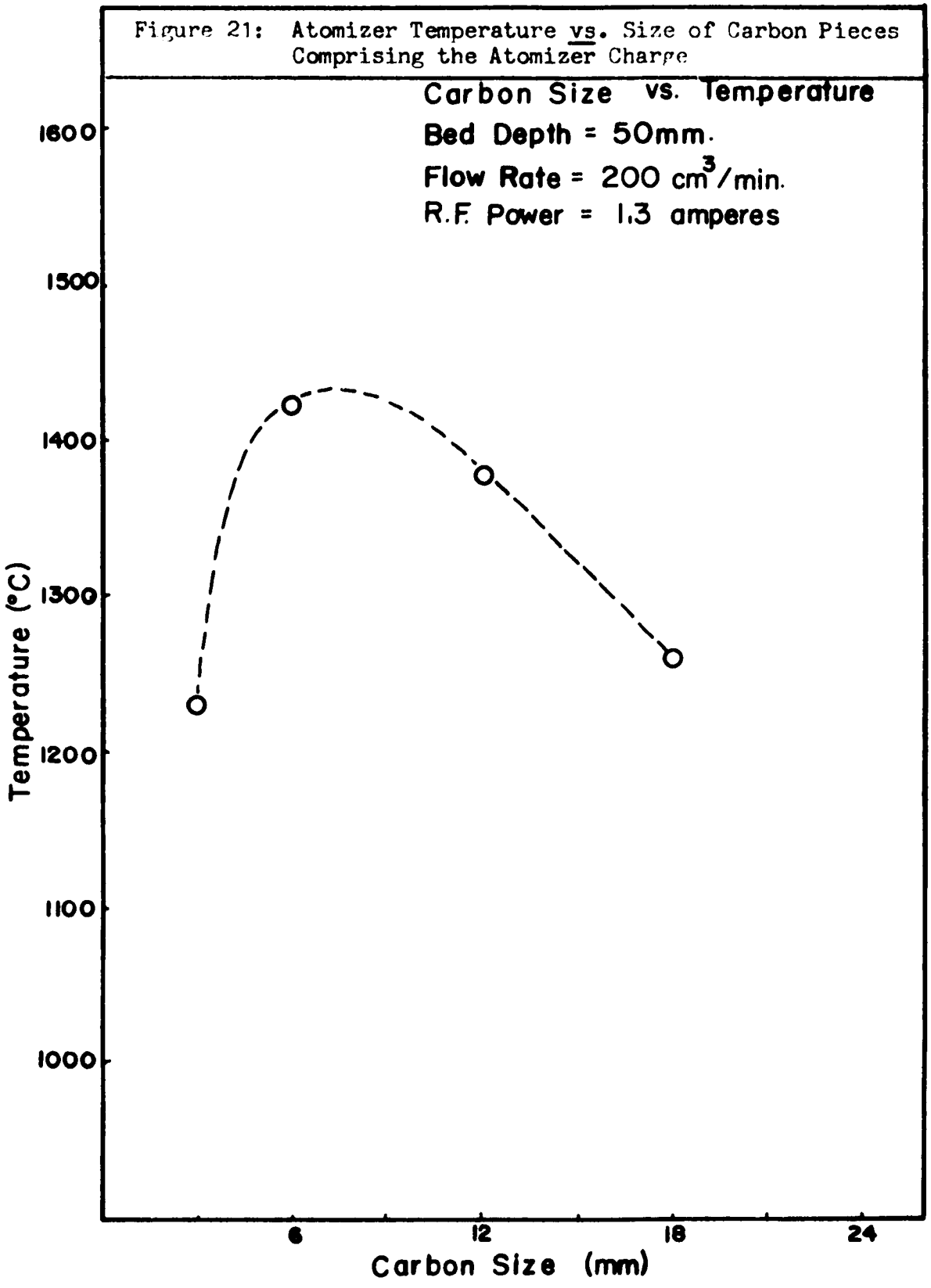
The data indicated that the temperature continued to increase with plate current for both the 50 mm. deep bed and for the 75 mm. deep bed, thus indicating no decrease in coupling efficiency. Indeed, for the 50 mm. deep bed, atomizer efficiency seems to increase, as the curve slopes upward.

The maximum plate current investigated was 1.3 amps, which was only 45% of the power the radiofrequency generator was capable of delivering. No higher plate currents were used because these higher currents would have resulted in temperatures higher than the melting point of the silica with which the absorption cell was built. It was not felt desirable to melt the cell.

The data also indicated that if an absorption cell could be built of materials capable of withstanding them, higher temperatures (and possibly greater atomization efficiency) might be attained.

It had been shown that the geometrical size of the individual pieces comprising the induction furnace charge had an effect on the coupling efficiency.[38] As the atomizer charge was made up of small pieces of carbon, and since the size of the carbon pieces would change as the upper layers of the carbon bed underwent combustion, it was necessary to determine the effect of carbon size upon temperature. Using a small lathe, cylindrical pieces of carbon of differing lengths were cut from 6mm. diameter spectroscopic carbon rods. The different lengths selected were: 3 mm.,6mm., 12mm., or 18mm. Sufficient pieces of each size were cut to provide a

Figure 21: Atomizer Temperature vs. Size of Carbon Pieces Comprising the Atomizer Charge



a 50 mm. deep bed composed entirely of pieces of that size. Each of the atomizer charges was placed in the radiofrequency field, and the temperature measured at constant plate current. These data are plotted in Figure 21. For a constant plate, current, maximum temperature was attained for a bed composed of carbon pieces 8 mm. in length. The shape of the curve was a perfect match for that curve derived theoretically to express the effect of geometrical size on coupling efficiency.[39]

The theoretically derived expression showed that the coupling efficiency was also frequency dependent, and that the coupling efficiency increased for smaller sizes as frequency increased. To illustrate the effect of frequency on coupling efficiency a qualitative experiment was carried out using a 3 megaherz induction generator which was available. Using the same carbon beds as had been previously prepared, the study of temperature vs. carbon size showed that maximum coupling efficiency occurred for a bed composed of carbon pieces of 3 mm. length. This experiment verified the frequency dependence of coupling efficiency of the carbon bed atomizer.

b. Effect of Temperature on Atomization: Since the effect of the various radiofrequency parameters had been determined, it was now possible to investigate the effect of temperature upon the formation of free atoms.

Accordingly, an experiment to determine the effect of temperature on atomization efficiency was undertaken. Injections of 2×10^{-11} grams of cadmium were made onto the carbon bed using the

direct drop technique. Injections were made at different temperatures on a carbon bed 50 mm. deep, composed of 13 mm. carbon pieces. The air flow-rate was maintained constant at 200 cm^3/ minute, and the atomic absorption signal monitored at the 228.8 nm. cadmium resonance line. The data are plotted in Figure 22. The data indicated that atomization efficiency increased with temperature for temperatures of 1000-1300° C., but levelled off at higher temperatures. It was not necessary to investigate temperatures lower than 1000° C. as the conversion of atmospheric oxygen to carbon monoxide was incomplete at temperatures at or below 900° C. It was anticipated that such incomplete combustion would reduce atomization efficiency greatly and make the instrument analytically insensitive.

c. Effect of Carbon Size on Atomization: For a given depth of carbon bed, the smaller carbon pieces could provide a greater surface area for interaction with the species being atomized, which should provide an increase in atomization efficiency. To investigate this possibility, 50 mm. deep beds were made up of carbon sizes 3 mm., 6 mm., 12 mm., or 18 mm., as had been done previously for the plate current studies. Each of these carbon beds was placed in the atomizer and brought to operating condition. Injections of 2×10^{-11} grams of cadmium were made onto each carbon bed, and the results recorded. The data are given in Figure 23. The data indicated a decrease in atomization efficiency with a decrease in carbon size. These data were puzzling because such an effect was exactly the opposite from that which would be expected on the basis of an increased surface area for atomization reactions.

Figure 22: The Effect of Temperature on Atomization of of Cadmium on the Carbon Bed

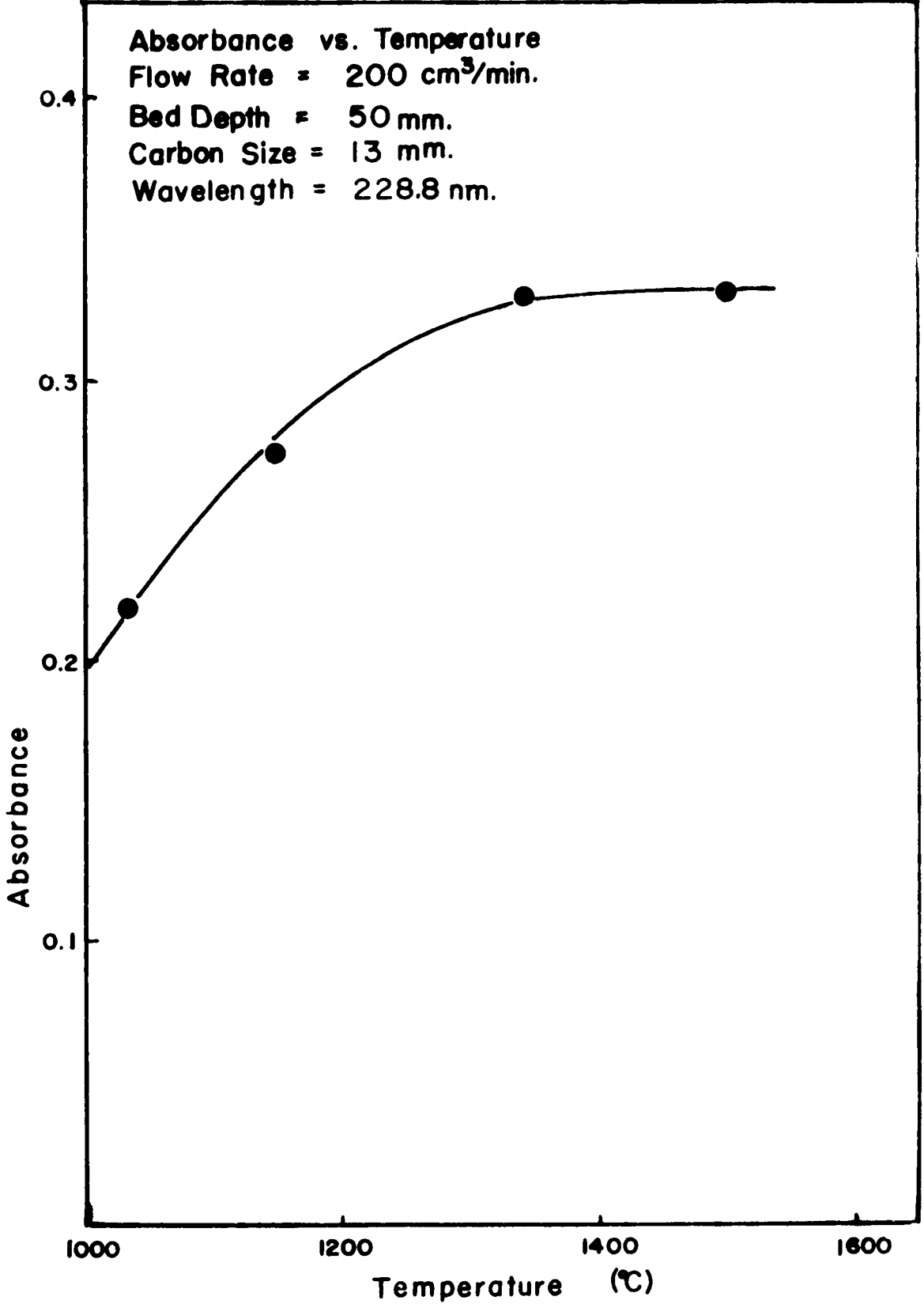


Figure 23: Effect of Carbon Size on the Atomization of Cadmium in the Carbon Bed

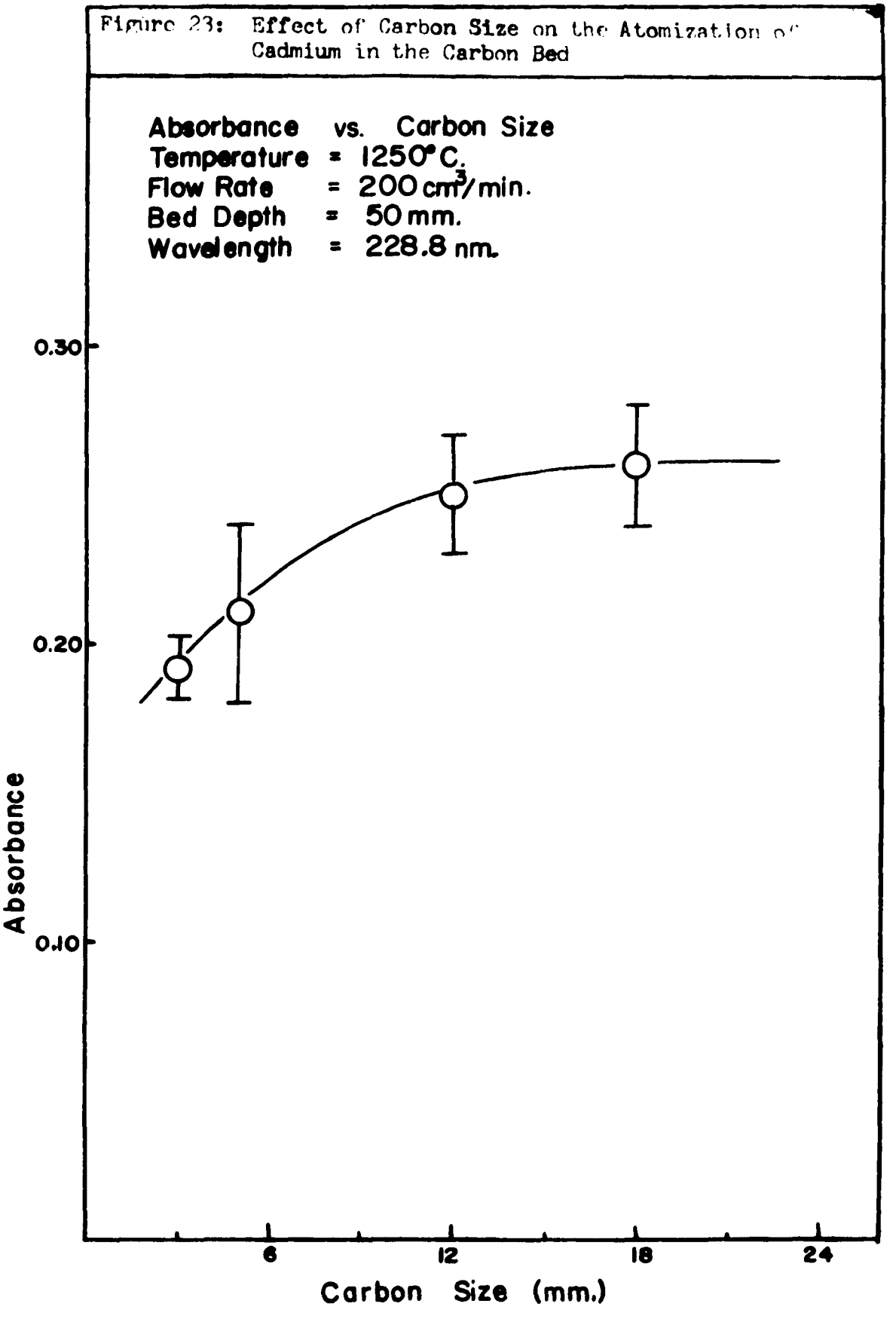
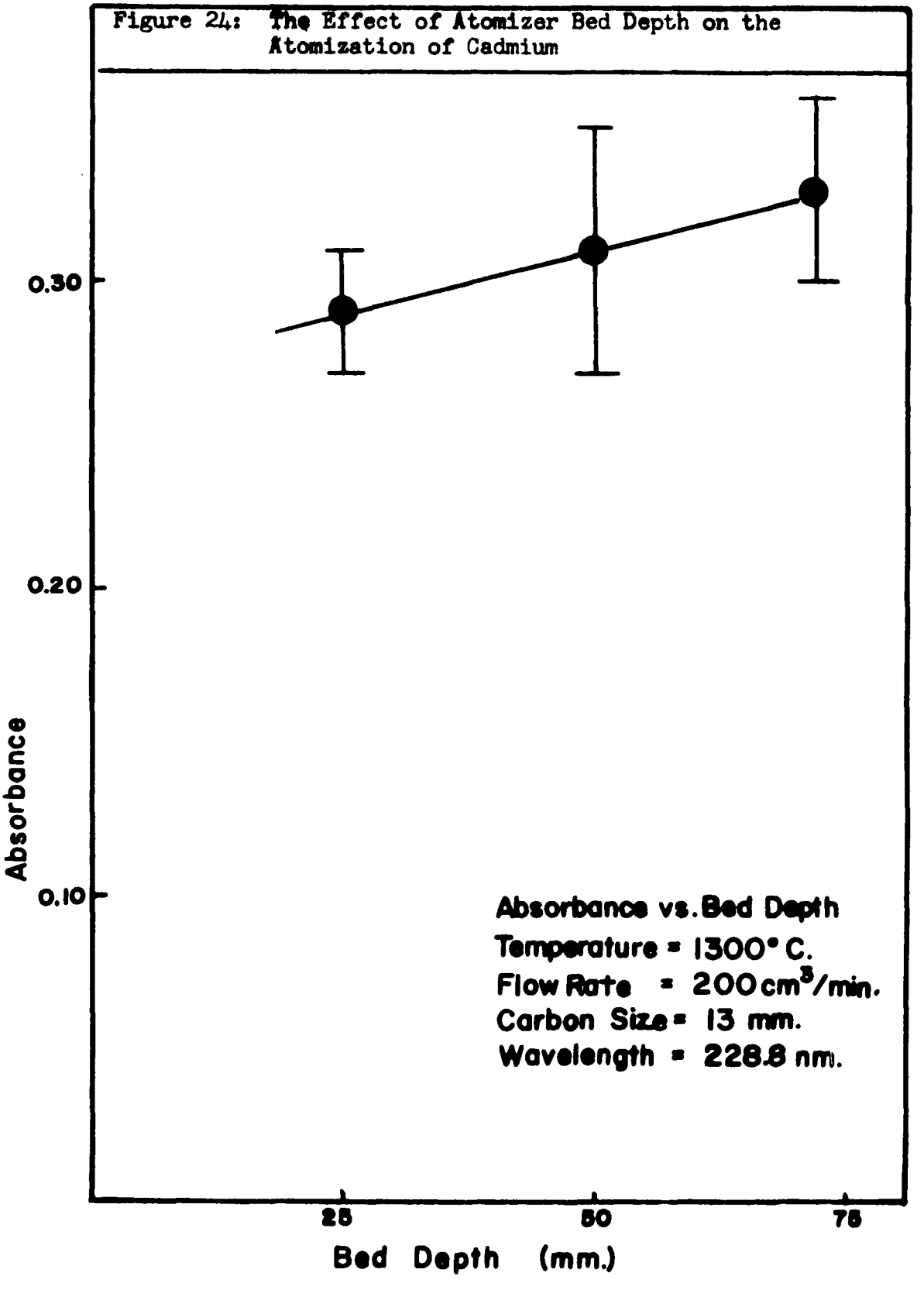


Figure 24: The Effect of Atomizer Bed Depth on the Atomization of Cadmium



d. Effect of Bed Depth on Atomization: As the carbon in the atomizer was burned during operation, two trends occurred: the size of the individual carbon pieces decreased, and the total depth of the carbon bed decreased. It has already been shown that the first trend resulted in a slight decrease in atomization efficiency. The next experiment was desighed to investigate the effect of the second trend.

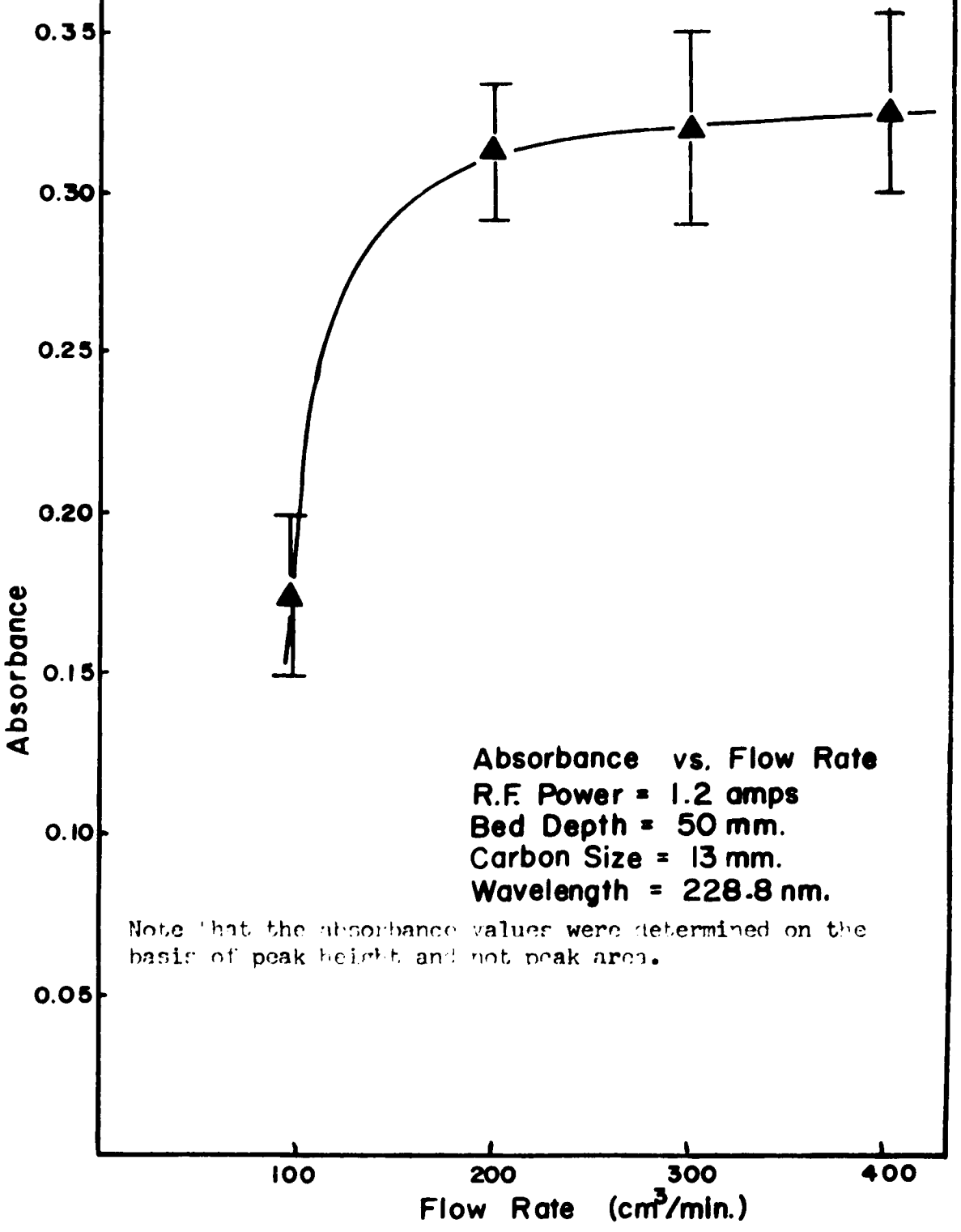
Accordingly, a 25 mm. deep bed of 13 mm. long carbon pieces was prepared and placed in the atomizer. Injections of 2×10^{-11} g. of cadmium were made onto the carbon bed and the data recorded. Additional carbon was added to bring the bed depth to 50 mm. and the radiofrequency power readjusted to maintain the temperature at the same level that had been used for the 25 mm. deep bed. Injections of 2×10^{-11} g. of cadmium were made onto this deeper bed. The bed depth was then increased to 75 mm. and the temperature again readjusted. The series of injections of cadmium were repeated upon the 75 mm. deep carbon bed. The data obtained are given in Figure 24. The data indicated that the atomization efficiency decreased only slightly with carbon bed depth. This trend would have little effect on the atomization efficiency as the depth of the carbon bed decreases only about 12 mm. during a four hour operating period.

e. Effect of Air Flow Rate on Atomization: The final parameter controlling atomization efficiency was the flow rate of air through the carbon bed. The flow rate, like carbon size and bed depth, governed the length of time the analyte spent in the hot carbon bed. An experiment to determine the effect of flow rate

upon the production of free cadmium atoms was therefore performed. With a carbon atomizer bed 50 mm. deep made up of 13 mm. long carbon pieces, injections of 2×10^{-11} g. quantities of cadmium were made onto the carbon bed at flow rates varying from 100 cm^3/ minute to 400 cm^3/minute, and the resulting absorption signals recorded. The results of this investigation were plotted in Figure 25 after being corrected for molecular background (see Section on Molecular Absorption). The graph indicated a severe decrease in absorbance with a decrease in flow rate from 200 cm^3/minute to 100 cm^3/minute. Such an effect would seem to be the opposite of what was expected, as a lower flow rate would increase the contact time with carbon, and thus increase the atomization efficiency. However, a glance at the actual absorption traces in Figure 26 showed the error in the interpretation of the data. The data in the graph were measured on the basis of peak height. The absorption traces immediately showed a great increase in peak area with decreased flow rates, thus indicating an actual increase in atomization efficiency. Several authors have discussed the greater accuracy involved when integrated areas were measured rather than peak heights.[40,41] Unfortunately, with the available instrumentation, there was no way to measure the peak areas correctly. The output of the amplifier was linear in percent transmission, and to properly measure peak area it was necessary to convert the signal electronically to linear absorbance.

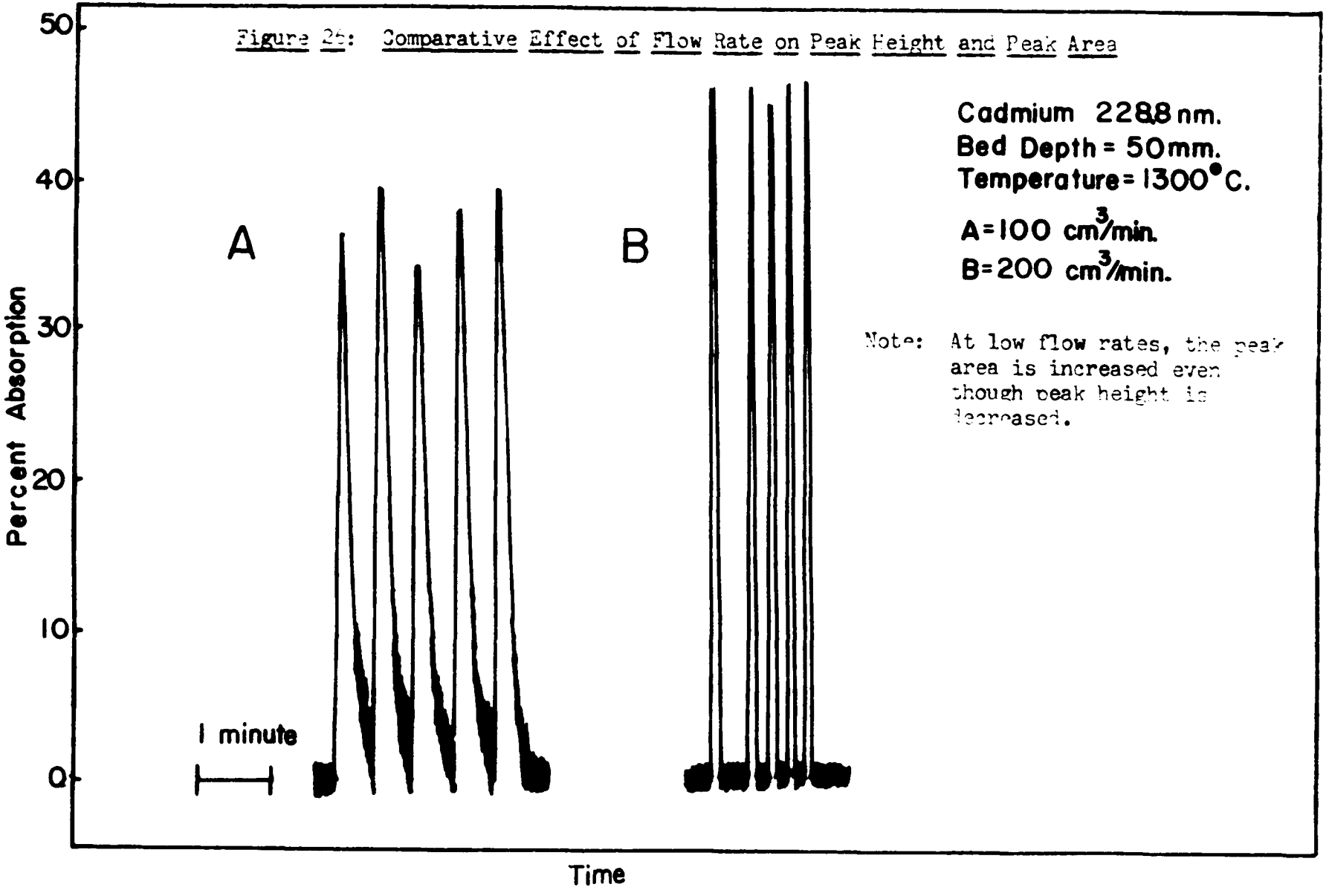
f. Carbon Bed Memory Effect: In all of the preceding work, whenever the carbon bed was replenished with fresh carbon, or a new carbon bed of "ultra-pure" carbon was placed

Figure 25: The Effect of Air Flow Rate on the Atomization of Cadmium in the Carbon Bed



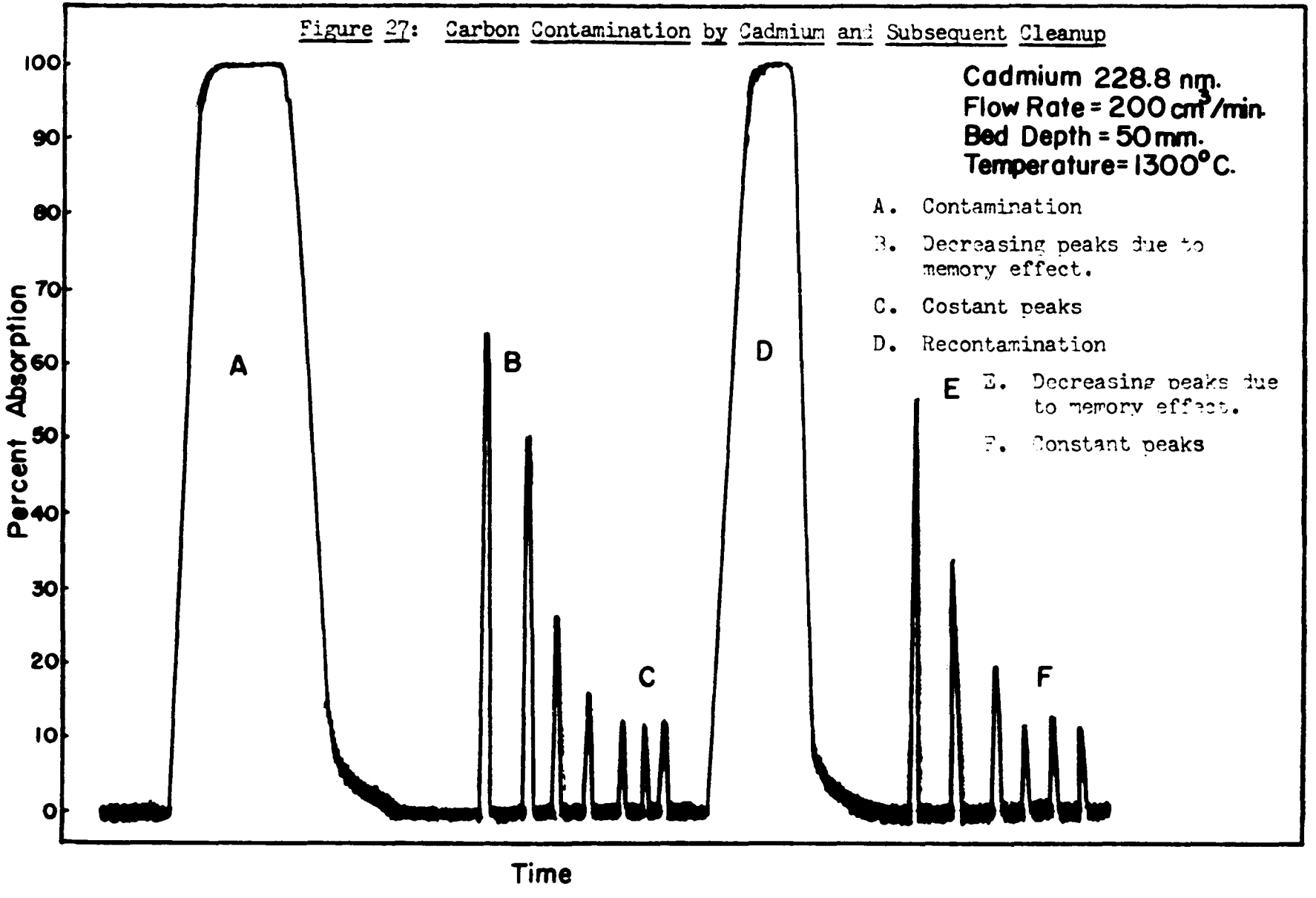
Note that the absorbance values were determined on the basis of peak height and not peak area.

Figure 25: Comparative Effect of Flow Rate on Peak Height and Peak Area



into the atomizer, the phenomenon shown in Figure 27 was noted. The first large peak, A, was attributable to cadmium contamination on the carbon rods. Such contamination had been reported previously by other workers in this research group.[42] However, after the cadmium absorption signal had evidently returned to baseline, and blank injections of "pure" water made onto the bed, the series of decreasing peaks B was noted (one peak per inject of water). The signals from "pure" water injections finally levelled off at a constant value C. There were two possible explanations for the phenomenon: a) the atomizer carbon surface contained active sites which had to be oxidized until the atom-producing ability of the surface was constant, or b) there was still a small amount of cadmium bleeding off of the rods, or some cold spot in the absorption cell, and which injections of water "steam-cleaned" until all cadmium was removed. A phenomenon similar to the above was noted in the use of the carbon filament atomizer of West, et al[43] and a hypothesis similar to a) advanced in explanation. In order to ascertain which of the two explanations was correct for the carbon bed atomizer, the carbon bed was re-contaminated by injection of 2 microliters of 1000 microgram/milliliter cadmium solution (2×10^{-6} g). Such an injection resulted in the absorption peak D. After the contamination signal had returned to baseline, blank injections of "pure" water were made, resulting in the series of decreasing peaks E. This again reached a constant peak height value F after several injections. The data indicated that explanation b) was the correct one for the carbon bed atomizer.

Figure 27: Carbon Contamination by Cadmium and Subsequent Cleanup

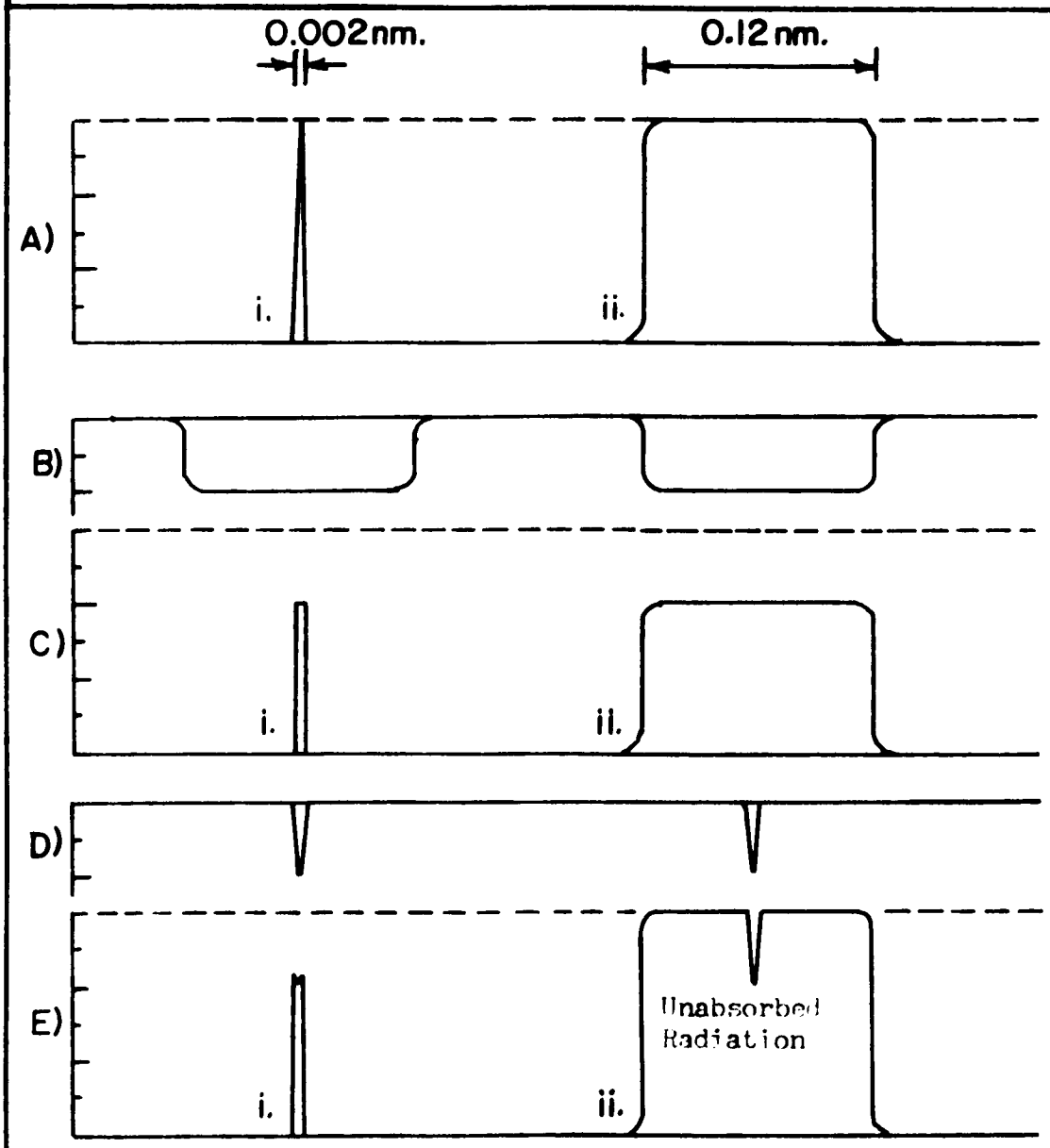


B. Factors Affecting Molecular Absorption Signal in Carbon Rod Atomic Absorption

1. Introduction: The effects of broadband molecular absorption had long been known to be an interference in flame atomic absorption spectroscopy[44] but were frequently ignored. It was the broadband molecular absorption of flame combustion products that restricted measurements in flame atomic absorption to wavelengths greater than 200 nm. unless special flames were used.[45] Broadband absorption may be caused by undissociated solvent molecules, flame combustion products, or undissociated salt particles, and had been observed for many different organic and inorganic matrices.[46,47] Molecular absorption was a function of both the particular molecular species under consideration, and of the portion of the spectrum being examined.[48,49] Molecular absorption by combustion products was found to be particularly severe for long-path flame adaptors.[50,51]

With the advent of non-flame atomic absorption, the problem of broadband, non-specific absorption was found to be of critical importance.[52,53,54] The effect of broadband absorption in atomic absorption spectroscopy is illustrated in Figure 28. The effects were illustrated for both atomic line radiation sources and broadband light sources and for the effect of atomic absorption and molecular absorption on each. The first instance was the comparative effect of molecular absorption on both the atomic line source and the broadband source (Figure 28C). In this case, the spectral line-width of the atomic emission line was of the order of 0.001 nm., while the spectral line-width of the broadband emission was equal

Figure 23: Relative Effects of Atomic and Molecular Absorption on Atomic Line and Molecular Emission Light Intensity



A) Unattenuated line (i.) and continuum (ii) radiation.

B) Molecular absorption profile.

C) Line (i.) and continuum (ii) radiation, attenuated by molecular absorption.

D) Atomic absorption line profile.

E) Line (i) and continuum (ii) radiation, attenuated by atomic absorption.

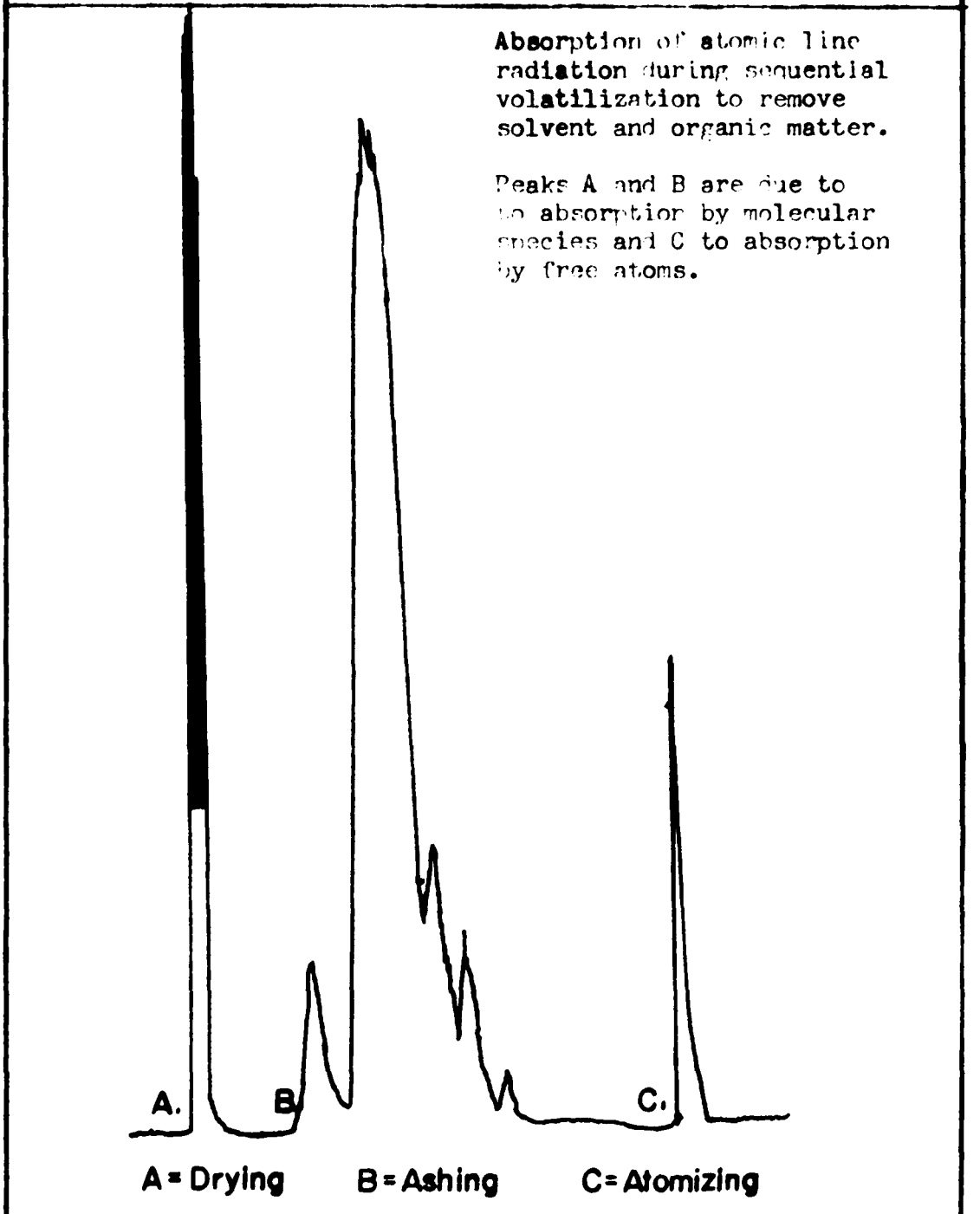
NOTE: The linewidth of the atomic absorption line is exaggerated for illustration.

to the spectral bandpass of the monochromator, or 0.12 nm. If a molecular species which absorbed light in the spectral region of interest was interposed between the source and monochromator, the effect on both the atomic line radiation intensity and the broadband emission radiation intensity would be the same. In contrast, the effect of atomic absorption on these two light sources was quite different. This difference is depicted in Figure 28. Since the width of the atomic absorption line was of the order of 0.002 nm., it was apparent that the effect of this absorption upon the total incident radiant energy of the broadband emission source reaching the detector would be negligible, while the effect on the atomic line source would be significant. These facts both illustrated the cause of the interference of molecular species in atomic absorption, and set forth a method of correction. Since the effect of atomic absorption upon broadband radiation was negligible, it sufficed to measure the molecular absorption with a broadband emission source and subtract this value from the observed total absorption signal. This approach had been used by many workers in atomic absorption spectroscopy[55,56] and is commercially available in several atomic absorption instruments.[57,58]

The compensation method of molecular background correction worked well, as long as one particular condition was met. This condition was that the concentration of molecular species not be great enough to absorb the entire atomic line. If the entire atomic line was absorbed by molecular species, the superimposed absorption by the free atoms would not be measurable, and correction techniques

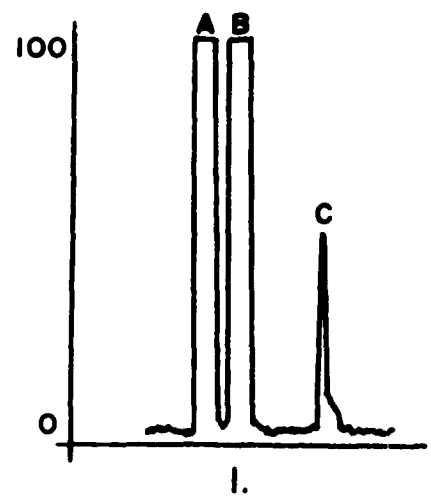
would no longer work. This situation was exactly what occurred in electro-thermal methods of flameless atomic absorption . The relative amount of analyte (metal compound) was so small compared to the molecular matrix, that the atomic line radiation was completely absorbed by the molecular species, and the superimposed absorption was not observable. This problem necessitated the use, in electrothermal atomizers, of some method of removing the molecular matrix. The usual means of accomplishing the matrix removal was by a process called "sequential" or "selective" volatilization.[59] In this technique, two or three separate heating steps were used (see Figure 29 and 30): a) drying- the electrothermal atomizer was heated to approximately 100° centigrade to drive off solvent, b) ashing- the atomizer was heated to 500-1000° centigrade to volatilize selectively any organic materials present, and c) atomization- the atomizer was heated to a temperature sufficient to cause thermal decomposition of metallic compounds into free atoms.[60,61] Unfortunately, the use of three steps introduced the possibility of metal losses during each step. To illustrate this possibility, consider each step: drying- the liquid sample might spatter during evaporation, or, if the analyte were sufficiently volatile (for instance, some of the metallic halides or organometallic species)it might be evaporated off; ashing- the remaining organic material might carry away some of the metallic material as it decomposed (i.e. by "covolatilization"),[62] and again, if the analyte was present as a compound not sufficiently volatile to be lost on drying, it might still be lost at the higher

Figure 29: Dry, Ash, and Atomize Steps in a Carbon Electrothermal Atomizer

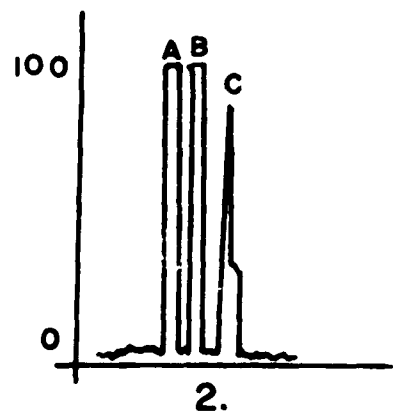


Determination of copper in milk using the Heated Graphite Atomizer and copper Hollow Cathode (derived from Reference 57)

Figure 9: Dry, Ash, and Atomization Steps in a Tantalum Electro-thermal Atomizer



1.



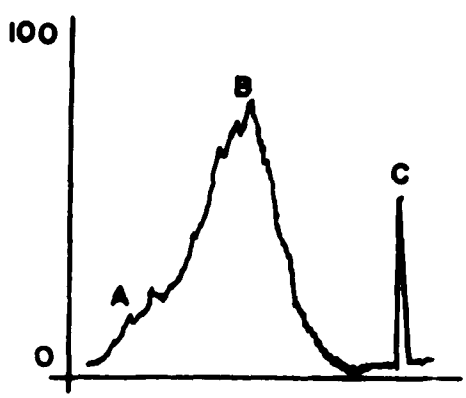
2.

Absorption Signals During:

A= Dry

B= Ash

C =Atomize



3.

Sample:

1. Serum manganese
2. Serum chromium
3. Blood lead

(derived from References 91 and 92)

temperature required for ashing; and atomization- in which the conversion of the remaining analyte was converted into free atoms, might result in a smaller atomic absorption signal as a result of losses during drying or ashing.

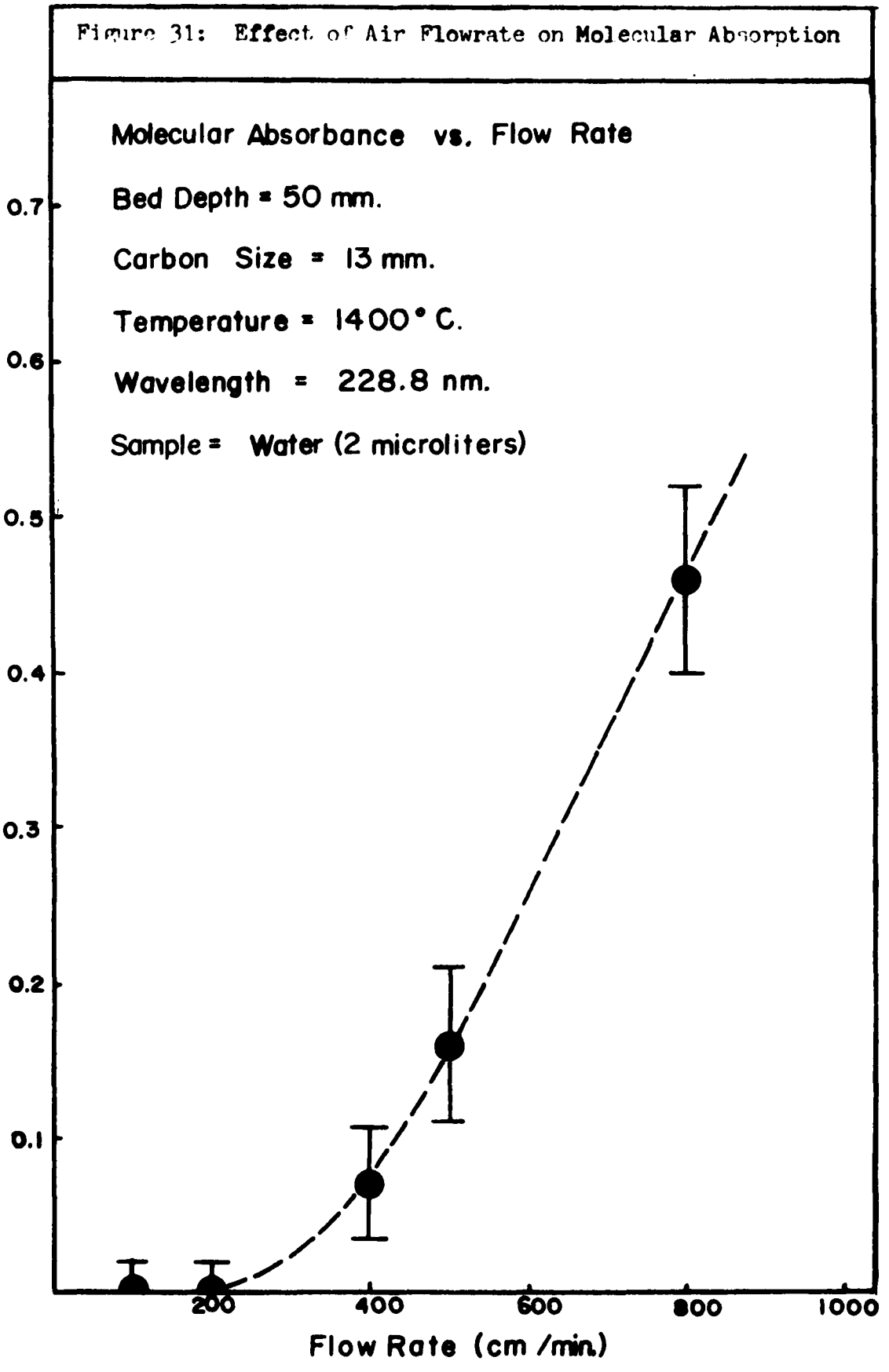
Since molecular absorption can cause such great interferences in atomic absorption spectroscopy, it was essential to investigate molecular absorption effects in the carbon bed atomizer. Accordingly, a series of experiments was undertaken to measure the molecular absorption caused by injection of several different matrices onto the carbon bed. It was also necessary to determine the effects of the operating parameters of the atomizer on the molecular absorption signal.

2. Experimental and Discussion:

a. Molecular Absorption of Aqueous Samples: Because the majority of samples in atomic absorption spectroscopy were aqueous it was decided that this matrix should be investigated first. Accordingly, samples of two microliters of deionized water were chosen as the sample matrix and injected onto the carbon bed using the Direct Drop technique (see Calibration Techniques Section) under different atomizer operating conditions. The light source used to monitor the molecular absorption signal was a deuterium discharge lamp.

As had been discussed in the section on factors affecting atomization efficiency, flow rate was an important variable, as it determined the contact time of the injected sample with the carbon bed. Accordingly, the effect of flow rate on molecular absorption was investigated. As was shown by the data plotted in Figure 31, molecular absorption was not detectable at or below flow rates

Figure 31: Effect of Air Flowrate on Molecular Absorption



of 200 cm^3/ minute, but increased rapidly as flow rate was increased past that level. This information could be interpreted on the basis of incomplete destruction of the solvent matrix. It was suggested that, under the atomization conditions present in the bed, the aqueous solvent underwent the following reaction:

$$H_2O + C \rightarrow CO + H_2 \qquad 6)$$

Equation 6), the well-known water-gas reaction, resulted in the formation of species which absorb only slightly or not at all in the UV spectral region. The fact that molecular absorption was observed with increasing flow rates indicated that reaction 6) did not go to completion and that intermediate combustion products such as OH• or H• were swept into the light path.

It was felt that the absorption coefficients of the reaction products were low over the wavelength range of analytical interest. Hence, it was necessary to confirm this assumption by experiment. Thus, beginning at 200 nm., injections of two microliters of water were made at intervals of 5 nm. throughout the wavelength range of the deuterium lamp out to 300 nm. These data were plotted in Figure 32. As was evident from the graph, molecular absorption was negligible over the entire spectral region except for a short span between 200 and 220 nm., over which molecular absorption increased. These data have since been confirmed by other workers in this laboratory during investigation of atomic absorption in the vacuum ultraviolet spectral region.[63] The molecular absorption could be attributed to the increasing absorption by hydrogen at wavelengths shorter than 220 nm.

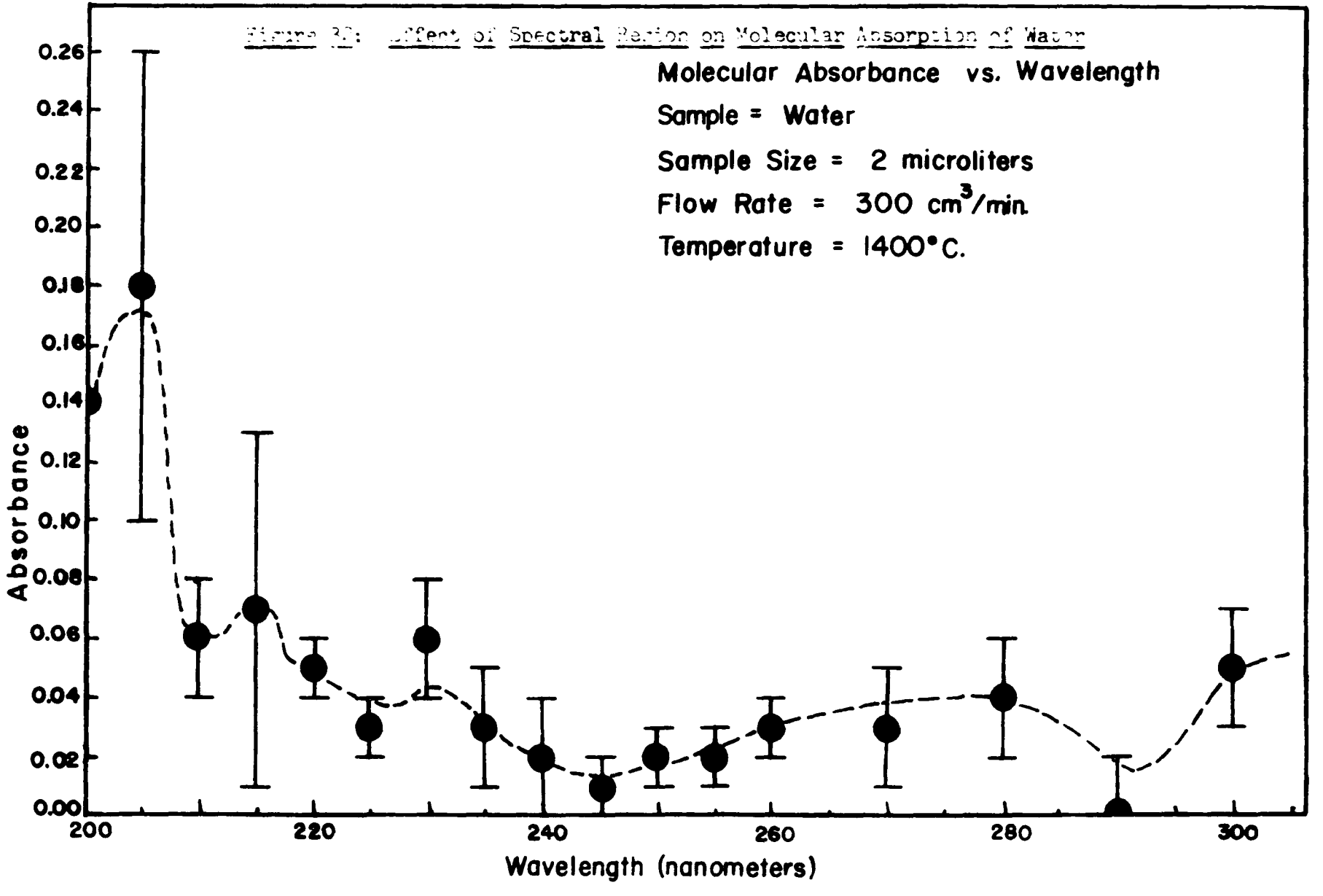


Figure 3: Effect of Spectral Region on Molecular Absorption of Water
Molecular Absorbance vs. Wavelength
Sample = Water
Sample Size = 2 microliters
Flow Rate = 300 cm³/min.
Temperature = 1400°C.
Absorbance
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
200
220
240
260
280
300
Wavelength (nanometers)

An important parameter in atomization was temperature. Temperature may also be important in the formation of absorbing molecules. Thus it was necessary to determine the effect of temperature on molecular absorption. At the wavelength of interest (cadmium 228.8 nm. resonance line) injections of two microliter quantities of water were made onto the carbon bed at various temperatures. These data were plotted and illustrated in Figure 33. As can be seen from the graph, the molecular absorption was constant over the entire temperature range examined. The data also indicated that the reactions responsible for the reduction of molecular absorption were not significantly affected by temperature variation at temperatures greater than 1300° centigrade.

The final parameter of importance in atomization was the depth of the carbon bed. This factor, like flow rate, determined the residence time of the sample in contact with the atomizer carbon. An experiment was carried out to determine the effect of the depth of the carbon bed on molecular absorption. The atomizer was loaded to a depth of 25 mm. with carbon pieces 13 mm. in length, and injections of two microliter samples of water were made onto the hot carbon. After the data were obtained, the depth of the carbon bed was increased to 50 mm. and the injections of water onto the bed repeated. Finally, the depth of the bed was brought to 75 mm. and the injections made. The radiofrequency power was adjusted with each change in bed depth to maintain the temperature constant at 1300° centigrade. The data, which were plotted in Figure 34, indicated an increase in molecular absorption with a decrease in carbon depth.

Figure 33: Effect of Temperature on Molecular Absorption by Water.

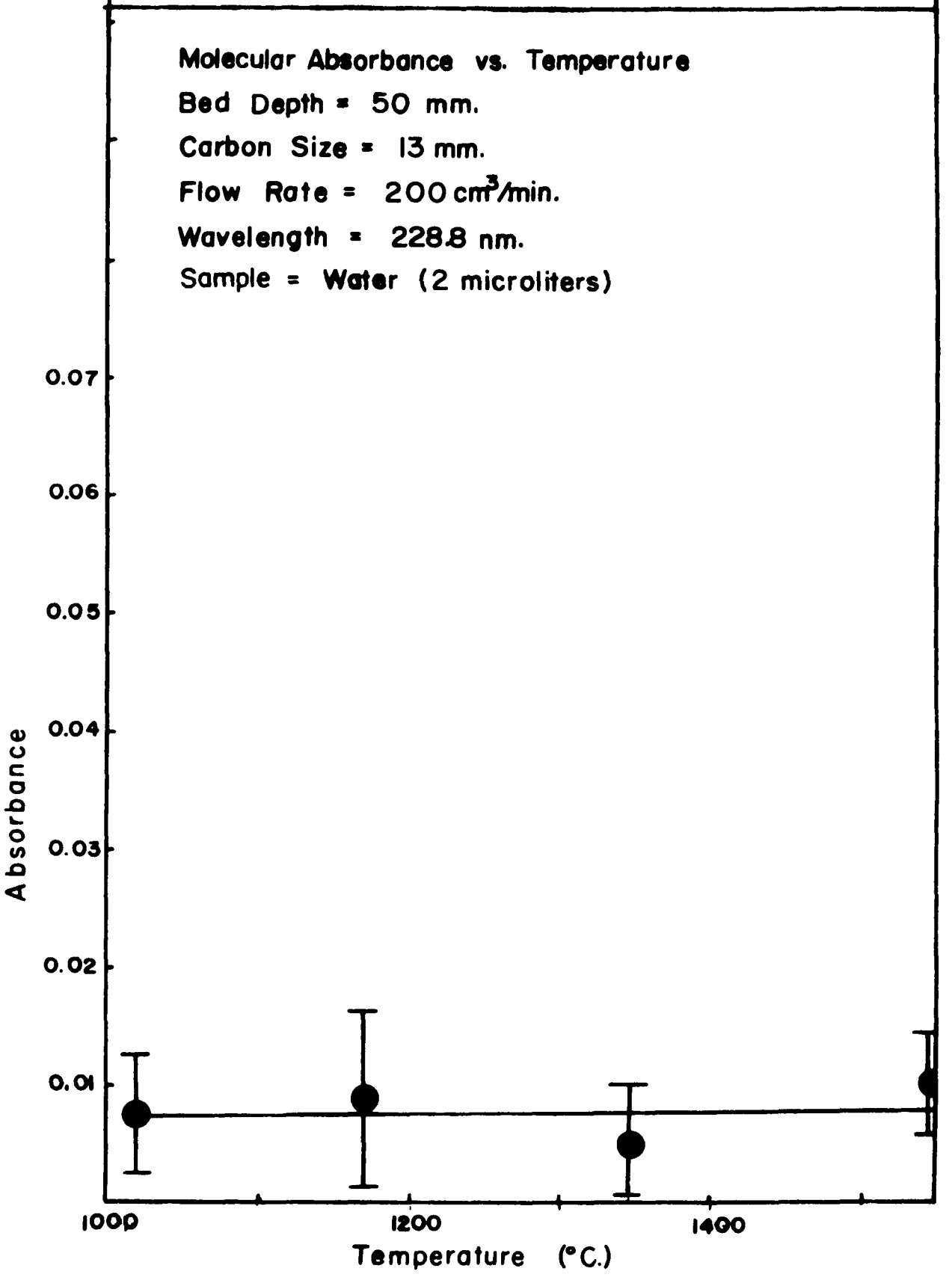
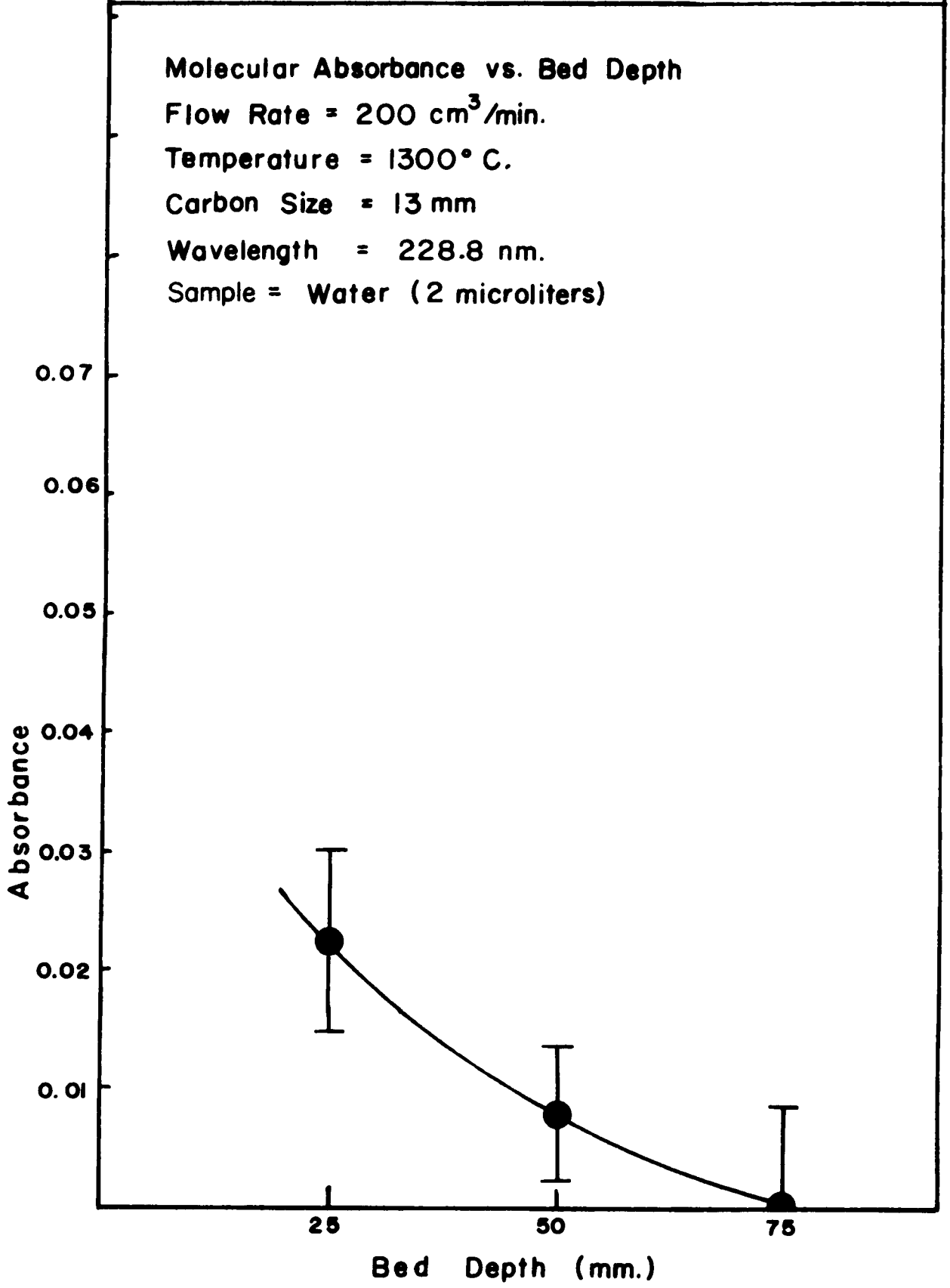


Figure 34: Effect of Carbon Bed Depth on Molecular Absorption by Water



These data were consistent with the data obtained about the effect of air flow rate on molecular absorption, and indicated that the time of contact with the hot carbon was the most important factor in reducing molecular absorption. It could be seen however, that even under the worst conditions, the molecular absorption signals were so small as to be easily corrected by the background correction technique.

b. Molecular Absorption of Organic or Biological Samples:

Since it was desirable to apply the Robinson flameless atomic absorption technique to samples other than aqueous, an investigation was undertaken into the molecular absorption interferences of organic and biological samples.

To determine the efficiency of reduction for organic species, the following synthetic sample was used. It consisted of a saturated sample of anthracene in benzene. It was felt that because of the great stability of aromatic ring structures and the tendency for incomplete combustion of such species, that molecular absorption due to combustion products from such a sample would be large. Consequently, injections of two microliter samples of the synthetic sample were made onto the carbon bed over the spectral region 200 to 280 nm. at 5 nm. intervals. The data were plotted in Figure 35. The data showed that absorption by molecular species was never greater than 0.10 absorbance units and could thus be easily corrected by a background correction technique.

It was felt that the lack of molecular absorption exhibited by organic matrices could best be explained by a reaction of the form:

$$C + O_2 + C_xH_y \rightarrow CO + H_2 \qquad 7)$$

That is, the organic matrix, in the presence of oxygen and hot carbon would undergo combustion, and the combustion products might be further reduced to carbon monoxide and hydrogen. These products exhibited low molecular absorption in the spectral region above 200 nm. This initial work has since been extended to other organic solvents by other workers in this research group.[64]

In the interest of air pollution analysis, and analysis of solid samples and biological matrices, it was felt that a study of the molecular absorption characteristics of filter paper was worthwhile. Filter paper was an extremely important sample. Air particulate samples were collected on it, solutions were filtered through it, and various liquids could be absorbed into it. If the molecular absorption from the sample were not too great, the avenue was opened for analyzing many different sample types using filter paper as the sample vehicle. Also, filter paper, being mainly cellulose, had basically the same chemical characteristics as most plant tissues, and a lack of molecular absorption would be an excellent indication that the direct analysis of biological tissues was possible. Such capability would be of great advantage in determining the health effects of trace metals. For these reasons, an investigation into the molecular absorption characteristics of filter papers was undertaken. At the optimum flow rate that had

Figure 35: Effect of Spectral Region on Molecular Absorption by Aromatic Hyrdrocarbons

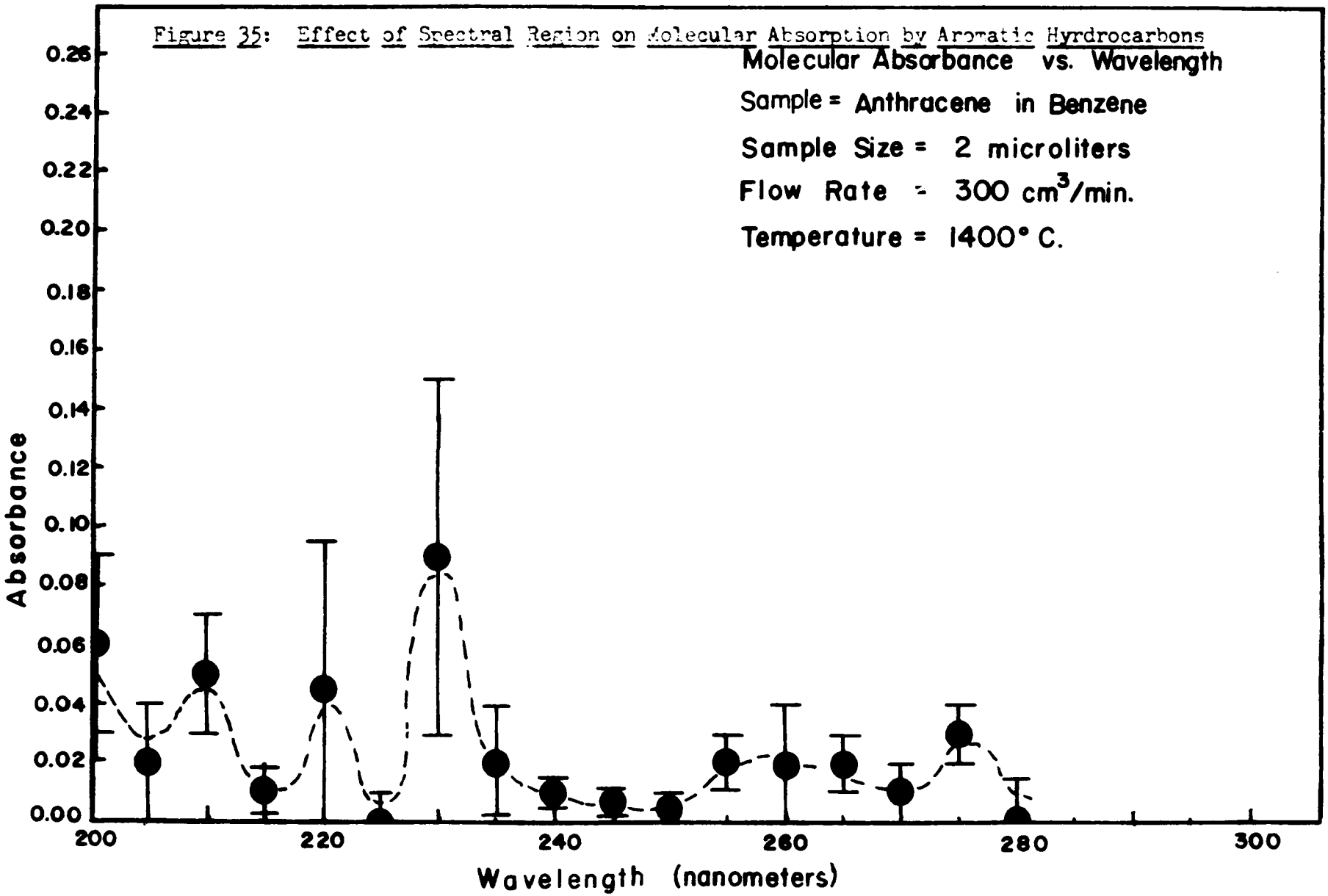
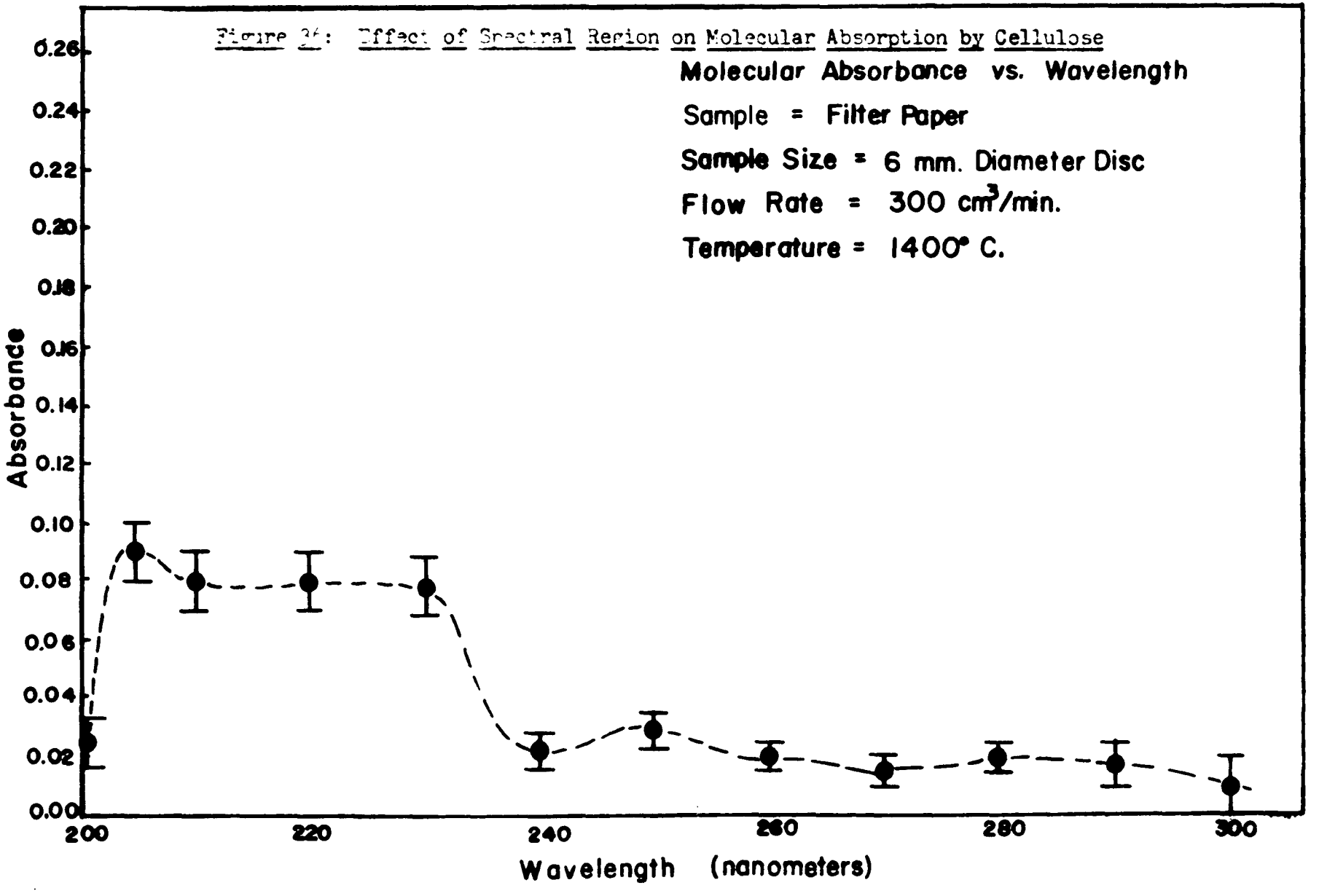


Figure 26: Effect of Spectral Region on Molecular Absorption by Cellulose



been previously determined for liquid samples, samples of filter papers of various sizes were dropped directly onto the carbon bed. The samples consisted of discs of 3 mm., 6 mm., 12 mm., or 18 mm. The data showed that there was little indication of molecular absorption at 228.8 nm. and that the amount of molecular absorption did not seem dependent on sample size. However, a visual observation of the combustion process showed that for samples larger than 12 mm. in diameter, a "flash-back" of combustion products up the atomizer sidearm occurred and introduced the possibility of sample loss. Consequently, no samples larger than 12 mm. in diameter could be used.

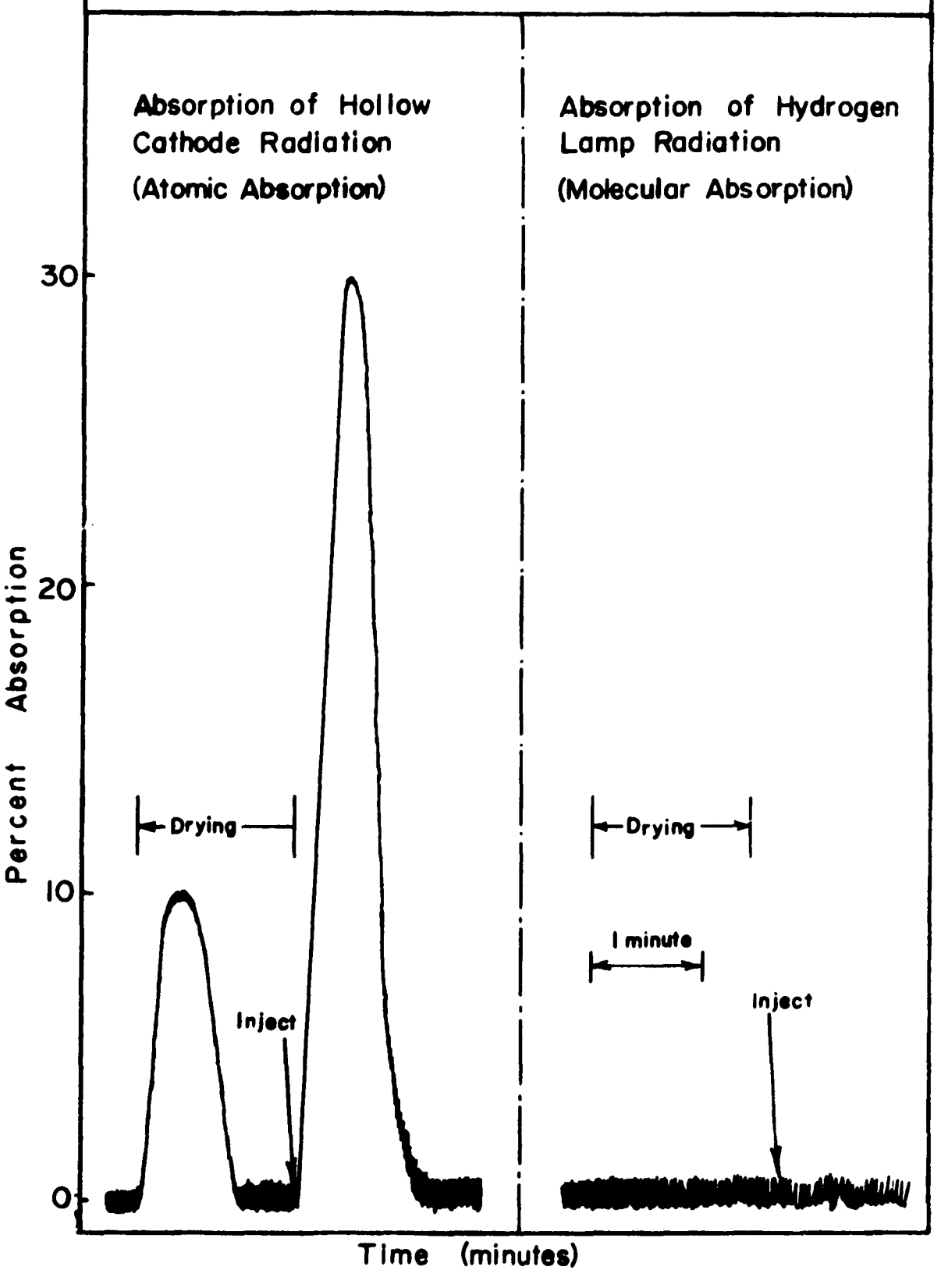
Since the filter paper was of biological origin, it contained elements other than carbon, hydrogen, and oxygen. Hence, its combustion products might have been of a different nature than those of water or organic solvents, which could give rise to molecular absorption in different spectral regions. To determine if such was the case, injections of 6mm. diameter discs were made onto the carbon bed at 5 nm. intervals throughout the 200 to 300 nm. spectral region. These data were plotted in Figure 36. The data indicated that molecular absorption was quite low for the spectral region above 240 nm., but was more severe between 200 and 240 nm. than was the case for water or the organic matrix. In any case, the molecular absorption was never greater than 0.10 absorbance units, and could easily have been corrected by an automatic background corrector.[65,66]

c. Sample Losses from Carbon During Heating Cycles:

In the introduction to the section on molecular absorption, it was mentioned that use of the various electro-thermal atomizers necessitated the utilization of a sequential volatilization technique to reduce molecular background. It was also mentioned that such sequential volatilization processes might result in a loss of metal sample during one or more of the heating steps. Such a possibility had been mentioned by some authors,[67,68] and indirect evidence had been obtained which indicated that such sample losses did indeed occur.[69] There had been, however, no direct observation of such effects. It was felt that the carbon bed atomizer offered a possibility of studying such sample losses directly, so an experiment was designed to investigate the phenomenon.

A small disc of carbon, 6 mm. in diameter by 1 mm thick, was impregnated with four microliters of 0.02 microgram/milliliter cadmium standard solution (8×10^{-11} grams). The carbon disc was then placed on the grid of the platinum loop liquid injector (discussed in Calibration Techniques) and lowered to within 50 mm. of the hot carbon. The carbon disc was heated by radiant energy from the carbon bed to simulate the drying step, and the carbon discs were dropped directly onto the carbon bed to accomplish atomization. If a controlled ashing step had been necessary, it could have been accomplished by heating the carbon disc with the platinum loop. In operation, the disc was lowered and the absorption signal monitored. As indicated by Figure 37, a large absorption peak was observed upon drying, which returned to base-line after about 30 seconds. The carbon disc was

Figure 27: Atomic and Molecular Phases During Solvent Evaporation from Carbon



then introduced directly onto the carbon atomizer bed, where its temperature rapidly rose to 1300° centigrade, thus volatilizing and atomizing any remaining sample. A second large absorption peak occurred during injection. There was a possibility that part or all of the absorption peaks noted were the result of molecular absorption by the matrix. Consequently, the atomic line source was replaced by the deuterium lamp and the experiment repeated. No molecular absorption was observed during either the drying period or after injection onto the carbon bed.

This experiment demonstrated quite vividly the tremendous possibilities for error that are inherent in the use of sequential volatilization techniques, and indicated the great control that must be maintained over the variables if such techniques were used. The fact that the carbon bed atomizer required no sequential volatilization for reduction of molecular background indicated a method by which volatilization errors might be avoided.

C. Observation of Atomic Absorption Signals from Ambient Air:

1. Pure Air System: For the quantitative determination of metal levels in ambient air, it was necessary to have something to which to compare the absorption signal from polluted air. This required a method of providing "pure" air free of metal compounds which might exist in molecular or particulate form. To this end, the clean air system described in the Equipment section was constructed (see page 27). As finally developed, the system consisted of a series of scrubbers and filters to provide air completely free of metal compounds. The scrubbing train consisted of: a) a drying column of calcium chloride, b) an adsorption column of activated charcoal, and c) a Millipore filter disc. The purpose of the calcium chloride column was to remove water vapor from the air-stream in order to prolong the adsorptive lifetime of the activated charcoal. Although it was known that water was preferentially displaced from activated charcoal by organic materials,[70] it was not known if a similar preferential displacement occurred for inorganic molecular species. The activated charcoal adsorbed organic or inorganic molecular pollutants from the airstream, although some particulate species might also have been removed. Previous workers in this laboratory had shown that activated charcoal was by far the most convenient and effective of the various scrubbing materials examined for removing metallic species from the air.[71] The final step in the purification of the air was its passage through a 0.45 micron-pore-size filter to remove any remaining particulate contamination. Since the work performed for this dissertation was completed, the single filter disc has been

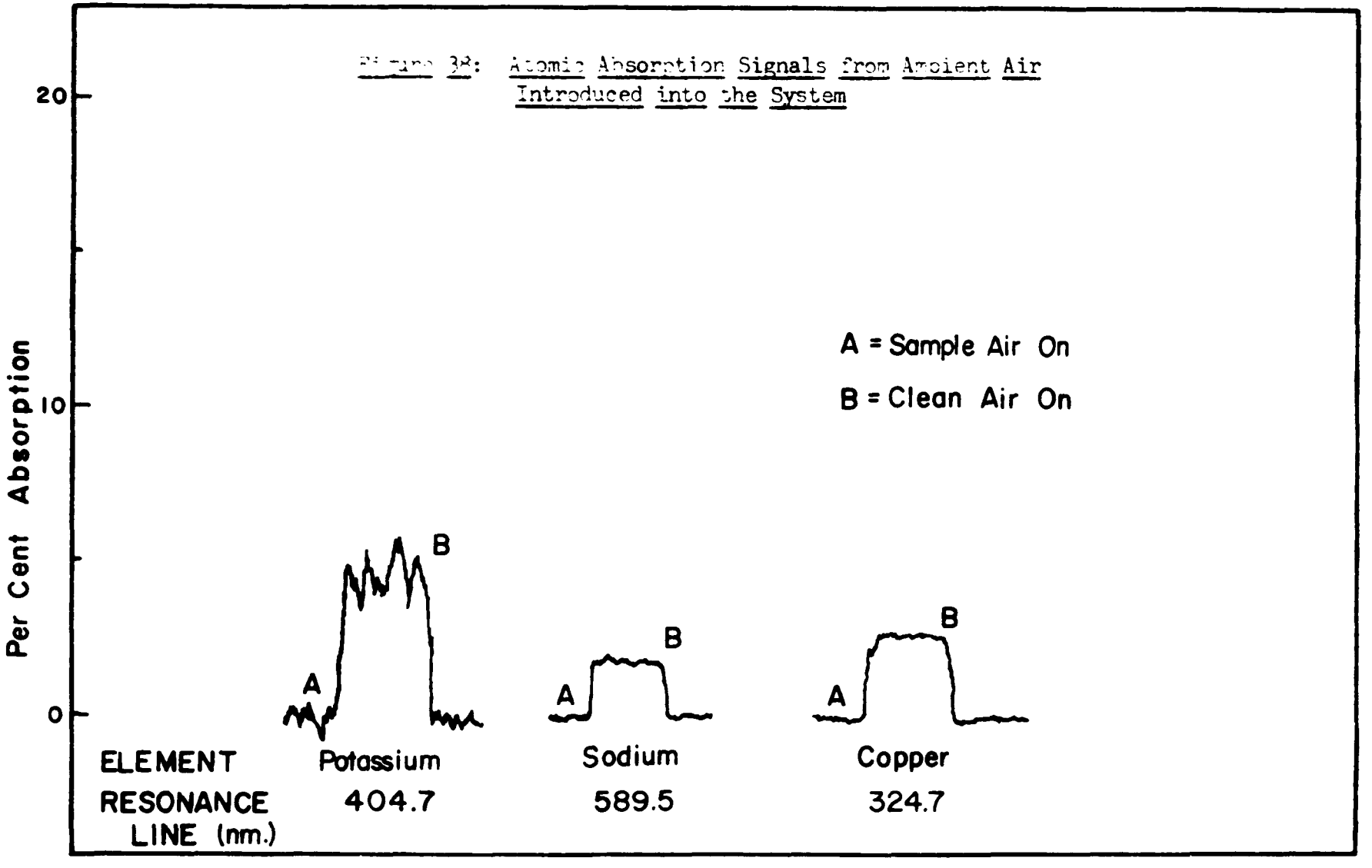
replaced by a series of filters of decreasing pore size: 8 microns, 1 micron, 0.2 micron, and 0.1 micron. The air flow progressed through the filters in the direction of decreasing pore size. The modification was undertaken to extend the lifetime of the filters without creating an excessive pressure-drop across any one filter. The new filtration train used controlled-pore-size polycarbonate filters from the Nuclepore Corporation.

Using the clean air system in the flow system mode in which an exhaust pump provided the driving force through scrubbing materials (described on page 24), ambient air signals were observed for sodium, potassium, arsenic, lead, selenium, copper, and zinc. These uncalibrated signals are reproduced in Figures 38 and 39. It was during this experiment that the decrease in air flow rate, presumably resulting from the resistance to flow provided by the scrubbing materials, was observed. This observation led to the re-design of the air flow system and resulted in use of air under pressure, which provided the force to drive air through the scrubbing materials. A compressed air tank was chosen as the source of pressurized air.

The modified air flow system was used to provide pure air in the study of the measurement of atomic absorption signals for the determination of cadmium in air. It was also used by other workers in the research group to measure atomic absorption signals for mercury in the ambient air.[72]

2. Atomic Absorption Signals from Ambient Air: Atomic absorption signals were obtained from the ambient air using the

Figure 38: Atomic Absorption Signals from Ambient Air Introduced into the System



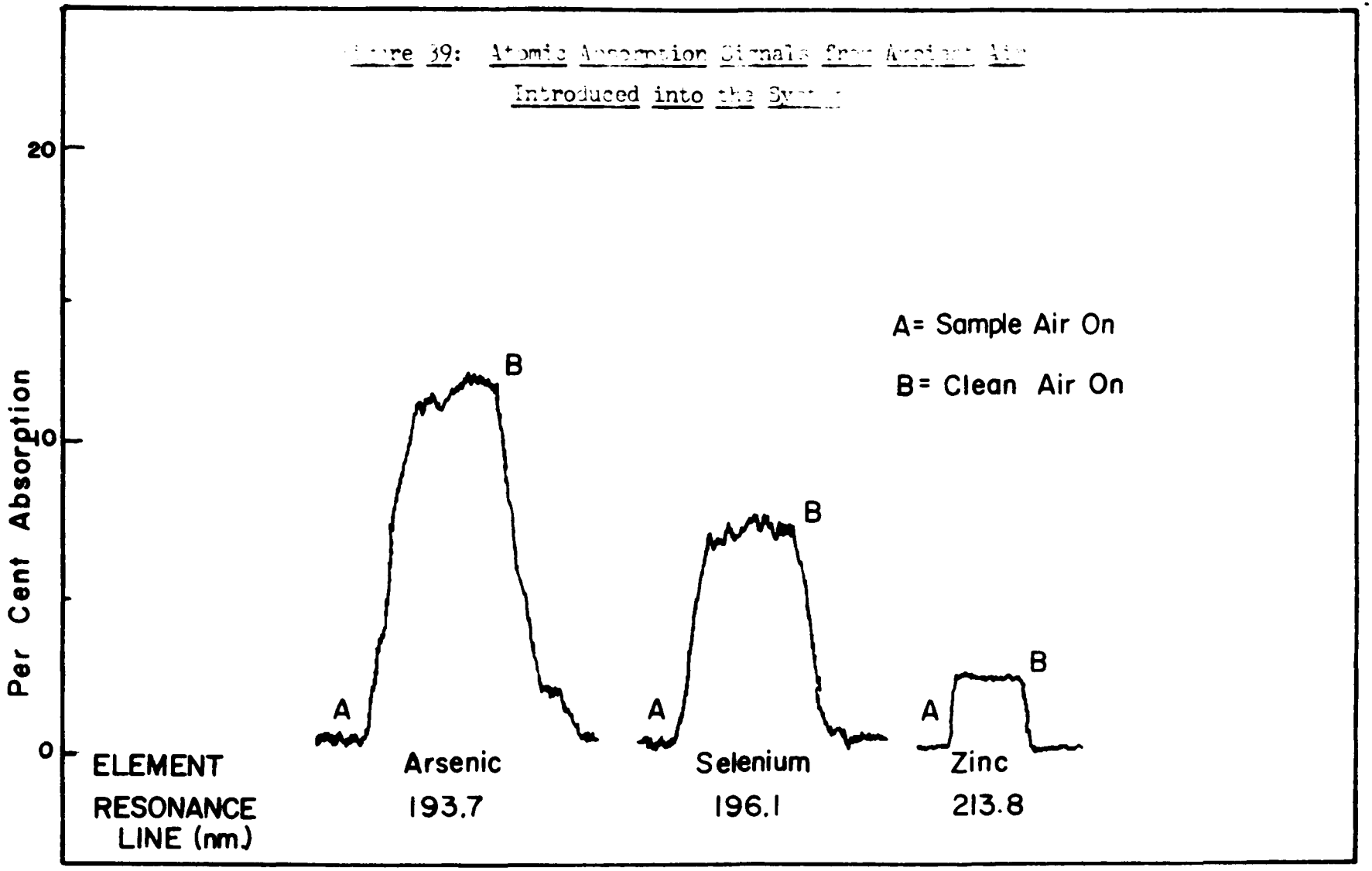
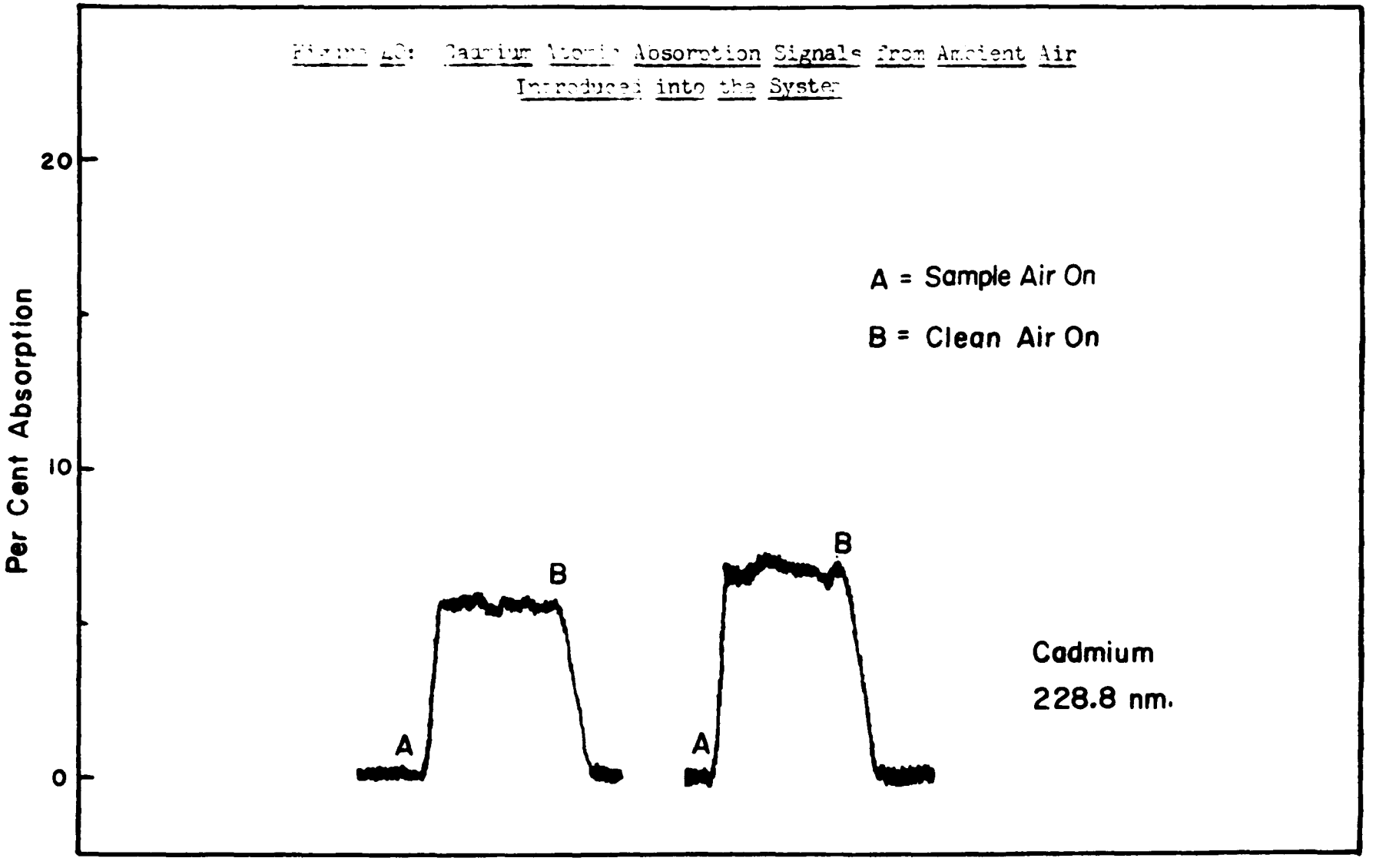


Figure 39: Atomic Absorption Signals from Ambient Air Introduced into the System

following technique. With clean air flowing through the atomizer, the instrument was turned on, allowed to stabilize, and 0 and 100% transmission limits set. This procedure established the base-line to which polluted air signals were compared. The clean air stream was then turned off, and the vacuum flow pump drew ambient air into the atomizer. If there was a detectable quantity of cadmium in the air, the signal rose to some value of absorption. The clean air stream was then re-routed through the atomizer to re-establish the baseline. Typical uncalibrated absorption traces for cadmium are given in Figure 40.

Uncalibrated absorption signals cannot be used to determine the concentration of pollutants in the atmosphere, even though they proved that the atomizer was efficient enough to produce a sufficient quantity of free atoms to produce an atomic absorption signal for the small amount of pollutants present. The absorption signal was indicative of the sensitivity of the method, but it was necessary to devise some means to calibrate the instrument in order to obtain quantitative data.

Figure 40: Cadmium Atomic Absorption Signals from Ambient Air Introduced into the System



D. Calibration Methods for Atomic Absorption:

1. Introduction: The necessity for calibration of any measurement system cannot be overstated, but the difficulties involved at the ultra-trace levels involved in air pollution were extreme. The magniture of the problem can be illustrated by the following calculation for one elemental pollutant, lead. The average ambient air concentration of lead in the United States was 0.8 micrograms per cubic meter.[73] Assuming that the volume of the light path of the instrument was 50 cm^3, a quick calculation showed that the quantity of lead that must be measured was 10^{-11} grams. In order to effect calibration of the system, acceptable accuracy and precision were necessary using these very small quantities.

Previous workers had used the techniques of diffusion tubes[74] and permeation cells[75] together with gas dilution techniques[76] to effect calibration of the spectrophotometer. For the measurement of lead and mercury, the calibrating materials used were tetraethyl lead and elemental mercury, respectively. Such techniques could be used for these elements because the calibrating materials possessed sufficiently high vapor pressures that air saturated with the vapors contained a significant quantity of the metals. Unfortunately, these techniques could not be extended to other metals due to a lack of available compounds with sufficiently high vapor pressures.

2. Experimental and Discussion:

a. High Temperature Volatilization Cell

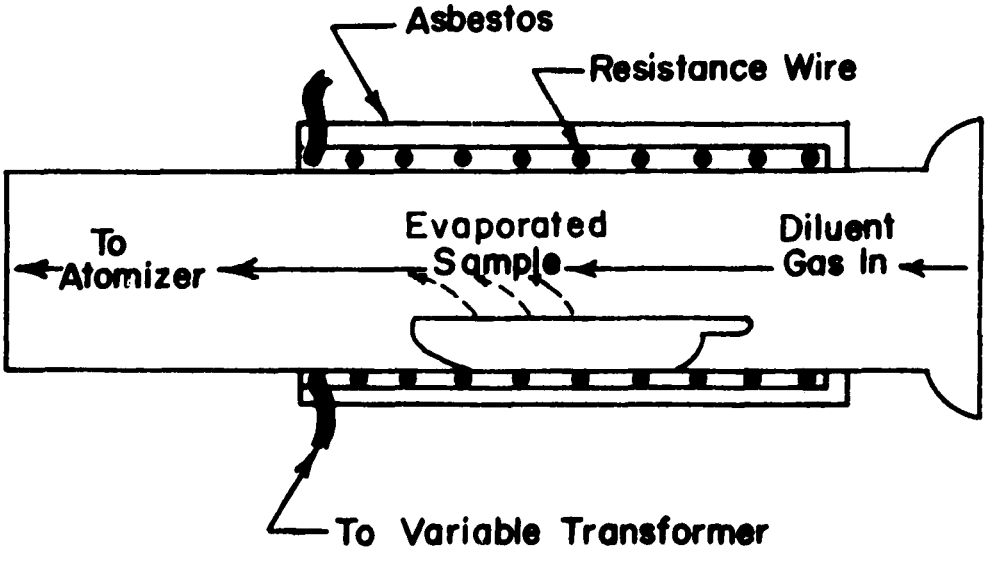
As previously mentioned, only a few compounds had a sufficiently high vapor pressure to be used at room temperature.

The number of acceptable compounds can be increased by working at an increased temperature with the consequently increased vapor pressures.[77] This approach had been used by previous workers in this laboratory to obtain calibration data for cadmium and to study anionic interferences for cadmium, lead, and mercury.[78] The compounds studied were: cadmium chloride, cadmium sulfide, cadmium sulfate, lead chloride, lead phosphate lead carbonate, mercuric chloride, mercuric sulfate, and mercuric nitrate.

In operation, the high temperature volatilization cell, shown in Figure 41, was set up in a hood with the appropriate metal or compound in a porcelain boat within the cell. The cell was brought to a suitable temperature and an airstream passed through the cell into a series of scrubbers for a period of some days. The scrubbing solutions were then analyzed by standard flame atomic absorption. From the concentration of metal in the solution, the air flow rate, and the time of air flow, it was possible to calculate the metal concentration produced. The calibrated volatilization cell was then placed at the inlet of the atomizer and the conditions of temperature and flow rate reproduced so as to obtain a calibration curve of absorbance vs. metal concentration.

Although the high temperature volatilization technique had been shown to provide worse precision than the permeation or diffusion techniques, it was felt that the technique possessed the requisite versatility to be useable for many elements. Consequently, an investigation was undertaken into the use of the high temperature volatilization cell using other metals as calibrating media.

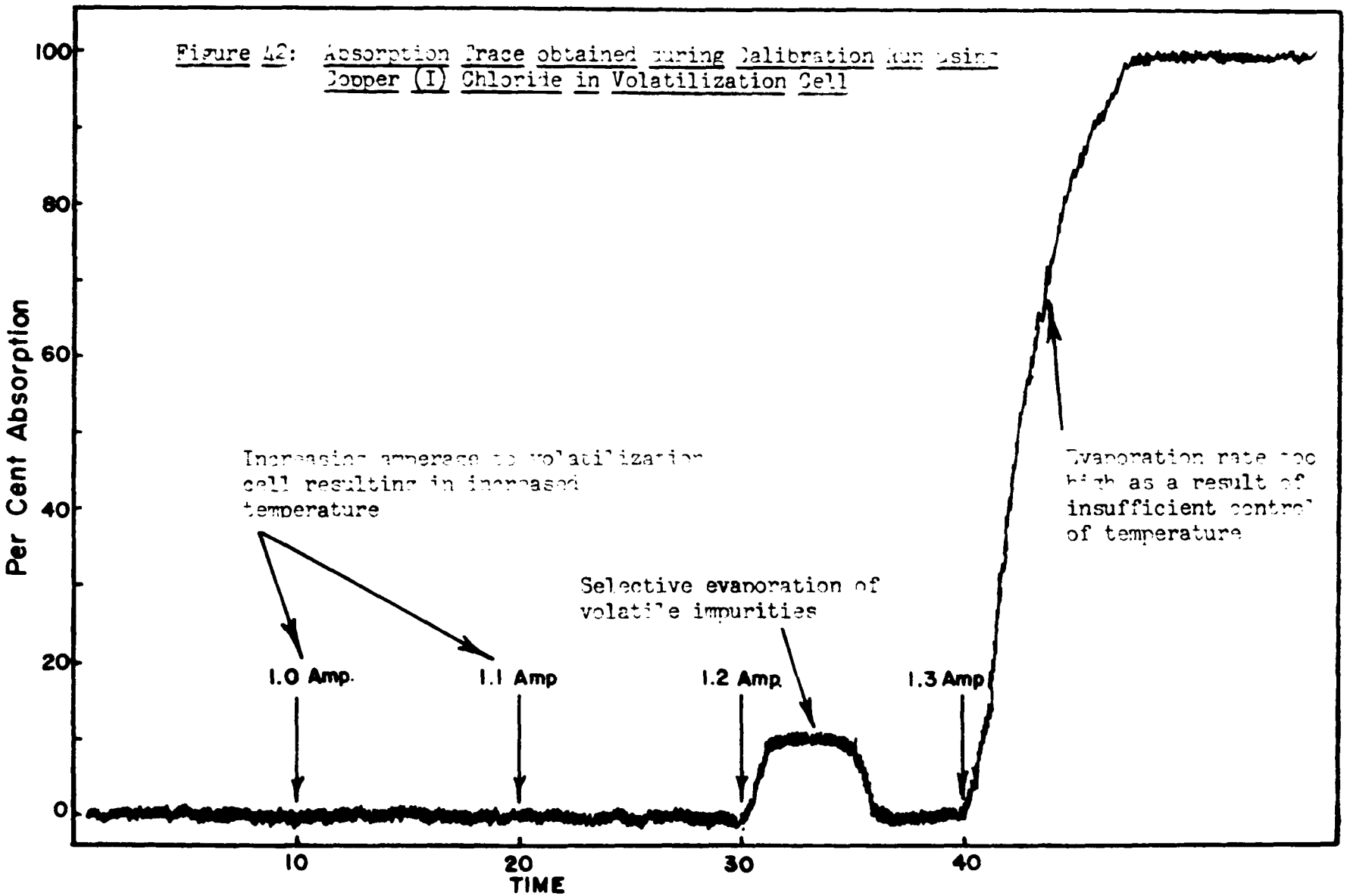
Figure 41: High Temperature Volatilization Cell used for Calibration Studies



High Temperature Volatilization Cell

At the time of this research, interest was centered on air pollution by copper, as atomic absorption signals had been obtained for copper in the ambient atmosphere. It was hoped to calibrate the instrument for determination of copper. In an initial attempt to record calibration signals, copper (I) chloride was placed in the volatilization cell. While monitoring the atomic absorption signal, the temperature of the cell was increased in stages until an observable absorption signal was obtained. The temperature was then held constant until the signal attained an equilibrium value. Surprisingly, as the temperature was maintained constant, the atomic absorption signal fell back to zero rather than attaining a constant value. Upon a further temperature increase, an absorption signal resulted which flooded the instrument, and did not return to baseline even after the volatilization cell had been removed from the atomizer. The absorption trace is illustrated in Figure 42. Visual observation of the material remaining in the porcelain boat indicated that the copper (I) chloride had decomposed into a black solid (evidently copper oxide). It was felt that the initial peak that fell back to baseline was due to the preferential volatilization of a low-boiling impurity in the copper (I) chloride. The contamination of the cell evidently occurred during the decomposition of the copper (I) chloride into copper oxide, with a large amount of copper being swept into the atomizer along with the gaseous decomposition products. It was felt that the difficulty might have been caused by a lack of sufficient temperature control at the higher temperatures available in

Figure 42: Absorption Trace obtained during Calibration Run using Copper (I) Chloride in Volatilization Cell



the volatilization cell. Consequently a more volatile copper compound (copper(I) iodide) was chosen for the next calibration attempt. The boiling point of copper (I) iodide was 1290°C. as opposed to 1490° C. for copper (I) chloride. Using the copper (I) iodide, the experiment was repeated, with the same results as had been obtained with copper (I) chloride. That is, decomposition to copper oxide and contamination of the absorption cell. In yet another attempt, copper acetylacetonate was chosen as the calibrating medium, as the metal acetylacetonates were quite volatile.[79] The same results were obtained as with copper (I) chloride and copper (I) iodide, i.e. decomposition to the oxide. Since all roads led to the oxide, it was decided to abandon attempts to use the lower temperatures available with the volatilization cell and to push it to its maximum in an attempt to use copper oxide as the calibrating medium. Thus, a pure sample of copper oxide was loaded into the volatilization cell and the temperature slowly raised. At the maximum temperature available (1000° C.) no atomic absorption was observed and attempts to calibrate the instrument for copper were abandoned.

Since many of the species used for calibration decomposed to oxides, it was decided to attempt calibration of the spectrophotometer for arsenic because arsenic oxides were quite volatile at low temperatures (As_4O_6 sublimed at 193° C.). Also, atomic absorption signals had been detected in the ambient atmosphere. Thus a quantity of arsenic trioxide was loaded into the volatilization cell and the temperature slowly increased. An absorption signal

was observed which rapidly rose to 100% absorption and failed to return to baseline after the volatilization cell was removed. The cell was washed with nitric acid to remove the contamination and the experiment repeated. The same results were obtained. It was decided that the difficulties entailed in use of the high temperature cell were too great to justify the investment of further time in attempts to make it work, and the device was abandoned. A search was begun for a new and more promising calibration technique.

b. Direct Introduction into the Atomizer of Standard Solutions on Carbon Pellets

Attempts were made to calibrate the instrument by impregnating microliter quantities of standard solutions onto carbon pellets. The latter were dropped into the atomizer, where atomization occurred and absorption measurements taken. The basis of the technique was as follows: liquids can be used as the calibrating medium, permitting the use of a wide range of concentrations, and hence a wide calibration range. On introduction of the impregnated carbon pellet into the atomizer, it would fall onto the surface of the carbon bed, where it would be rapidly heated. The rapid heating would volatilize the standard solution, which would traverse the atomizer bed and be reduced to its constituent free atoms. The free atoms thus formed would flow into the light-path and give rise to an absorbance "peak" which could be related to a continuous absorbance from air.

An experiment to test such a technique was begun by machining small pellets of carbon (6 mm. diameter by 0.5 mm thick) from rods of ultra-pure spectroscopic carbon.

After machining, several of the pellets were tested for cadmium contamination by injection into the atomizer. The pellets were found to be highly contaminated with cadmium as large absorption peaks were recorded upon injection. Since the spectroscopic carbon rods were known to contain an organic binding material, it was felt that the absorption signal might have been due to broadband molecular absorption. To test this possibility, the cadmium hollow cathode was replaced by a deuterium discharge lamp and the injections repeated. Although absorption signals were recorded using the continuum source, they were much smaller than those that had been recorded using a cadmium hollow cathode. Thus it was evident that the carbon pellets were contaminated with cadmium. In order to use the pellets for calibration, they had to be cleaned of cadmium. The best method available for removing the cadmium contamination was to heat the carbon pellets in the radiofrequency furnace. Therefore, the carbon pellets were loaded as the lower three-quarters of an atomizer charge, then covered over with regular atomizer carbon for the remaining one-quarter of the atomizer bed. Such an arrangement was necessary to prevent air oxidation of the carbon pellets during the conversion of atmospheric oxygen to carbon monoxide. It had been visually observed that oxidation occurred only in the upper 13 mm. of the carbon bed. After loading, the radiofrequency generator was turned on and the carbon pellets heated to 1500° C. The cadmium absorption signal was monitored during heating and when it had returned to baseline, the carbon pellets were removed, allowed to cool, and stored in a air-tight polyethylene vial. The cleaned

pellets were tested for contamination at a later date and found to give a blank reading of 0.05 absorbance units, which indicated minimal recontamination. An examination of the molecular absorption characteristics of the cleaned pellets indicated that the heat treatment had resulted in complete elimination of the organic binding material and the resulting molecular absorption. It was suggested that the small atomic absorption signal might have been due to cadmium adsorption from ambient air during transfer and storage.

Calibration was attempted using the pre-cleaned carbon pellets. Two microliter samples of cadmium chloride standard solutions were syringed onto the carbon pellets (2×10^{-10} grams total cadmium) and the pellets injected into the atomizer. Blank injections of non-impregnated pellets were also made. The data obtained were listed in Table 1. The experiment indicated that, although there was a large signal difference between the impregnated pellets and the blank pellets, the precision was so poor as to preclude the possibility of obtaining useful calibration data. In particular, it was noted that the extent to which the standard solution soaked into the carbon pellet had a great effect on peak height. For those pellets in which there were numerous hair-line cracks (these were a result of machining operations), the peak height was much reduced.

A similar result relating peak height to carbon porosity was noted by workers using the carbon filament atomizer.[80]

Table 1

Introduction of Solutions on Carbon Pellets

Sample	Atomic Absorbance
1. Blank Chip	0.055
2. Blank Chip	0.051
3. Blank Chip	0.055
4. Blank Chip	0.042
5. Chip + 2 x 10^{-10} g. Cd	0.771
6. Chip + 2 x 10^{-10} g. Cd	0.496*
7. Chip + 2 x 10^{-10} g. Cd	0.656*
8. Chip + 2 x 10^{-10} g. Cd	0.958

* Denotes chips that were visibly porous

(Note the high sensitivity but poor precision for the cadmium samples)

It was felt that the precision might be improved by obtaining carbon pellets of constant porosity, but such uniform pellets were not available, so the method was discarded.

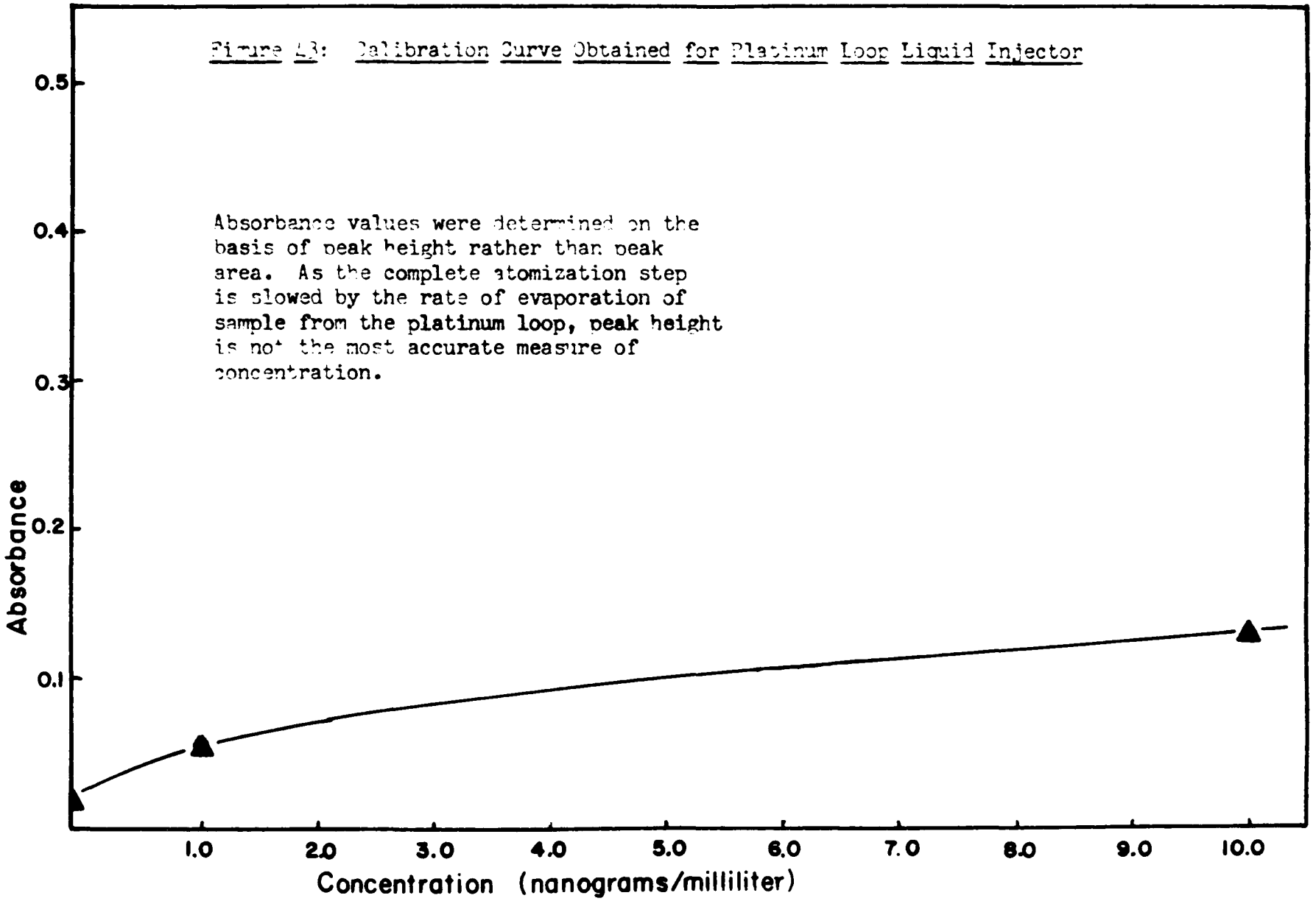
c. Platinum Loop Injector

The platinum loop liquid injector was designed in another attempt to use liquid standard solutions to calibrate the system for air analysis. It was thought that direct introduction of liquid samples would give rise to a molecular absorption signal so large as to obscure the atomic absorption signal. Such behavior was characteristic of the other flameless techniques. The platinum loop was designed to avoid molecular absorption interference by allowing a step-wise heating procedure to first drive off the solvent and then volatilize the calibrating species into the atomizer.

In operation, samples were syringed onto the loop with a Hamilton microliter syringe. The loop and sample were then lowered into position at a point 50 mm. above the carbon bed. The solvent was allowed to evaporate off at a temperature of about 150° C. After the solvent had been removed, the platinum loop was heated to 1600° C. by an electric current. Such a high temperature was used to volatilize off the metal salts remaining after removal of the solvent. The volatilized salts were carried into the hot carbon bed by the flowing air-stream where they were reduced to free atoms. An absorbance peak would then be recorded.

Calibration was attempted for cadmium using the platinum loop injector. A series of four microliter samples of cadmium

Figure 43: Calibration Curve Obtained for Platinum Loop Liquid Injector



standard solutions were introduced into the atomizer using the technique. The results were plotted in Figure 43. The calibration curve was extremely flat and the precision of injection was poor, although it was better than had been obtained using the carbon pellet technique. Monitoring the molecular absorption signal as the platinum loop was operated gave no absorption peak as the solvent was evaporating. This anomaly was the first indication that the molecular absorption characteristics of the carbon bed atomizer were not the same as other non-flame atomization techniques. At any rate, as it was attempted to undertake further studies with the platinum loop, an accidental short circuit disabled the injector. During the interval in which the platinum loop device was being repaired, a different calibration technique was tried which proved so successful that the platinum loop technique was abandoned, and the new technique used throughout the rest of this work.

d. Direct Drop Liquid Injector

As had been previously mentioned, monitoring the molecular absorption while using the platinum loop injector had given no indication of any broadband absorption. This occurrence was unusual because molecular absorption was so severe with electro-thermal atomizers. From this datum, it was decided to investigate the severity of molecular absorption when liquid samples (aqueous) were injected onto the top of the carbon bed. The breakdown of the platinum loop injector provided the opportunity to carry out the experiments.

While monitoring the molecular absorption with a deuterium light source, injections of deionized water were made directly onto the carbon bed. At an air flow rate of 200 cm^3/min., injections of four microliters of deionized water gave peaks of only 5-10% molecular absorption.

It was immediately apparent that the low molecular background that appeared during the direct injection onto the carbon bed opened the route to a simple, rapid, universal, calibration technique.

An experiment was undertaken to obtain an atomic absorption calibration curve using the direct drop technique. A new sampling head had been designed to hold the Hamilton syringe as injections were made onto the carbon bed (Figure 16, Equipment Section). Monitoring the atomic absorption signal as injections of deionized water were made onto the carbon bed indicated that, although the absorption peaks were large, they were quite variable. Visual observation of the syringe needle as injections were made immediately indicated part of the answer. The liquid drops were either hanging up on the syringe needle by surface tension, or striking the sidewall of the absorption cell rather than the carbon bed.

The problem of surface tension was solved by modification of the syringe needle from a septum penetration point to a pipette point (discussed in Equipment Section).

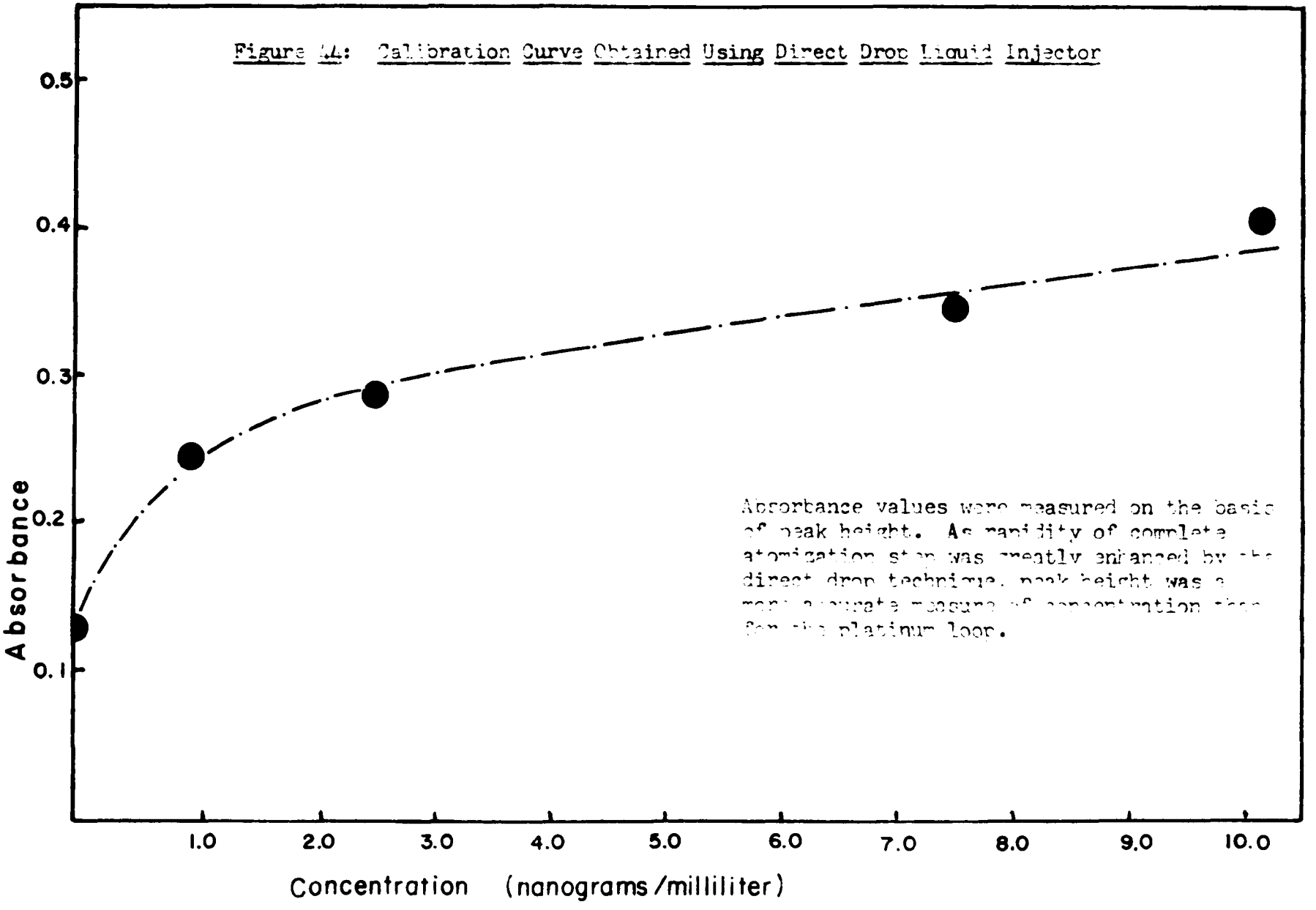
In order to avoid having the liquid drop strike the absorption cell wall, two modifications were made: a) the sampling head was modified to hold the syringe more rigidly, and b) the atomizer side-arm was shortened from 360 mm. to 200 mm.

Shortening the atomizer sidearm necessitated water cooling the sleeve adaptor to avoid thermal decomposition of the sealing "O" rings by radiant heating. The water cooling worked well, maintaining the sleeve adaptor at 50° C. though it was only 50 mm. from the 1500° C. carbon bed.

After the instrumental modifications were completed, the attempt to obtain a calibration curve was repeated. Samples of cadmium in concentrations of 10^{-6} to 10^{-9} grams per milliliter were made up and injected onto the carbon bed. The data obtained were plotted in Figure 44. The calibration curve was not linear, but the non-linearity of calibration curves at extremely low concentrations has been noted by other researchers and was not entirely unexpected. At such low concentrations, impurities not normally detectable gave large absorption signals and created serious blank problems. The precision of the data was 10% r.s.d., but the error was felt to be due largely to an inability to inject a reproducible volume of liquid onto the carbon bed with the Hamilton syringe.

The direct drop technique had several advantages over the other calibration methods tried: a) any soluble compound of reasonable purity could be used, b) impurities did not effect the calibration appreciably, as they might in volatilization techniques (by preferential volatilization), c) standards of different

Figure 14: Calibration Curve Obtained Using Direct Drop Liquid Injector



concentrations were easily prepared in liquid solutions, and d) calibration was extremely rapid.

The major disadvantage was that the calibration data was obtained as a series of absorbance peaks, relating grams of metal to a peak height (this difficulty was also present for the carbon pellet and platinum loop techniques) rather than a constant absorbance reading relating to an air concentration in micrograms per cubic meter. The relationship between peak height and ambient air concentration is discussed in the next section.

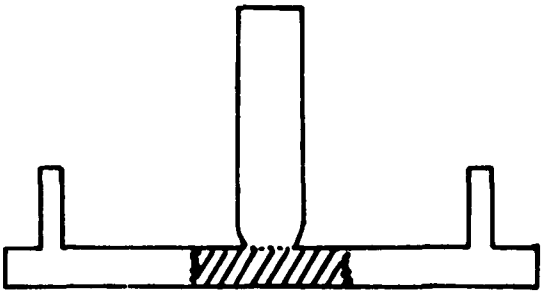
c. Relating Peak Height to Ambient Air Concentration

A calibration curve relating peak height in absorbance to cadmium concentration could be converted to a calibration curve relating absorbance to ambient air concentration if certain assumptions were made. These assumptions were: a) atomization efficiency was equal for the "pulse" injection resulting in absorbance peak and for continuous injections, and b) all free atoms which were contained in the injection "pulse" entered the light path and contributed to the absorbance peak before any were swept out of the cell by the flowing airstream. The situation for both "pulse" injection and continuous injection are pictured in Figure 45.

If the assumptions were valid, then the basic equation of atomic absorption:

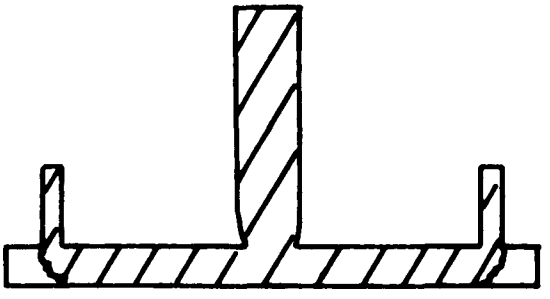
$$\int K_\nu d\nu = \frac{\pi e^2}{mc} N_1 f \qquad 1)$$

Figure 45: Illustration of Free Atom Distribution During "Pulsed" and Continuous Injection



A. "Pulse" Injection - Light Path Contains N Atoms

High concentration of atoms contained in a small plug.



B. Continuous Injection - Light Path Contains N Atoms

Low concentration of atoms distributed throughout the absorption tube.

where:

K = absorption coefficient at frequency v
e = charge on electron
m = mass of electron
c = speed of light
N_1 = number of atoms available to absorb
f^1 = oscillator stringth of absorbing line

indicated that the situations depicted in Figure 45 were equivalent, as the number of atoms (N_1) in the light path was the same. Hence, the ambient air concentration could be calculated by dividing the number of grams of material injected by the effective volume of the light-path.

That such an approach to obtaining a concentration was valid was shown by several factors. The first factor related to the relationship in time between the observation of an absorbance peak and the sample flow rate through the cell. If the effective volume of the light-path were 50 cm^3, and the flow rate of air through the cell were 200 cm^3/minute, the residence time of free atoms would have been approximately fifteen seconds. As the maximum absorbance values were recorded in 1-3 seconds after injection, it seemed safe to assume that all atoms had entered the light-path.

A second factor was the data obtained on the dependence of peak height on flow rate (Figure 25, page 51), which indicated that, above 200 cm^3/minute, the absorbance signal was independent of flow rate, thus indicating that all atoms must have contributed to the absorbance peak before any were swept out of the cell.

Using the preceeding technique, a calibration curve was calculated for the concentration of cadmium for the various injections

of standard solutions by dividing the absolute number of grams of cadmium injected by the effective volume of the light path. The calculated curve is given in Figure 46. Using the calculated curve, it was possible to obtain numerical concentrations from the absorbance signals obtained for cadmium in the ambient air. The values obtained for ambient air concentrations were listed in Table 2.

Thus it was apparent that a method of calibration had been developed which satisfied all ot the requirements for making ambient air measurements. The technique was rapid, inexpensive, and of essentially universal application. It also eliminated many of the difficulties encountered with volatilization, permeation, and diffusion techniques.

Figure 46: Calculated Calibration Curve for Determining Ambient Air Cadmium Concentration

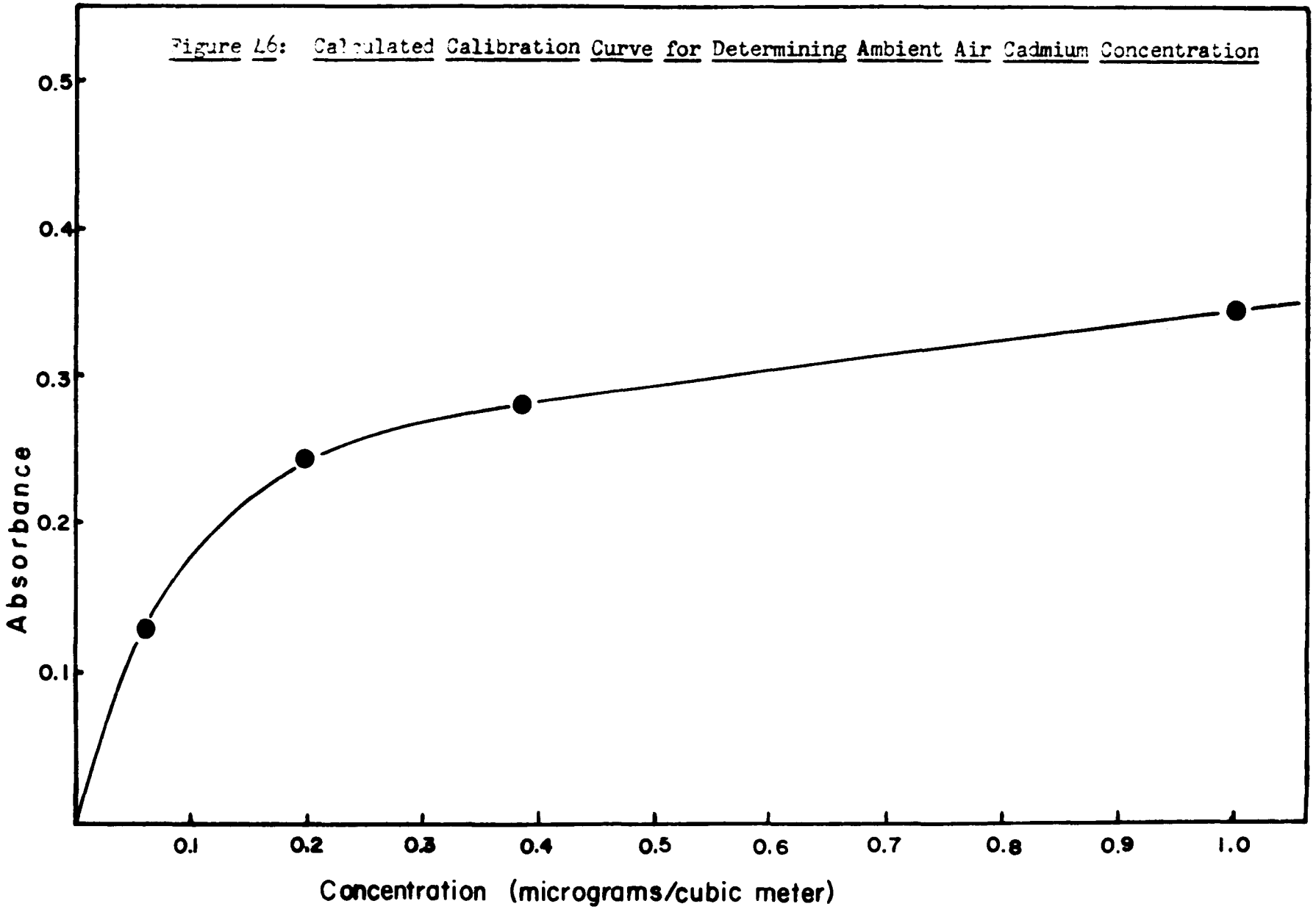


TABLE 2

AMBIENT AIR CADMIUM LEVELS

Sample Date	Absorbance	Concentration*
August 24, 1972[a]	0.027 ± 0.005	0.020 ± 0.004
August 26, 1972[b]	0.044 ± 0.005	0.035 ± 0.005

*expressed in micrograms per cubic meter

[a] immediately after heavy rain

[b] weather hot, clear, and sunny

E. Direct Analysis of Water Samples:

1. Introduction: As had been previously mentioned, the modificaitons of the atomizer to be mounted vertically rather than horizontally had a profound effect on extending the capabilities of the carbon bed atomizer. Some of the results discussed in the calibration techniques section were a direct result of this modification. These new techniques permitted the use of liquid solutions for calibrating the instrument for air analysis. It was immediately apparent that any system capable of using liquids for calibration purposes was also capable of directly analyzing liquid samples. It was decided to extend the investigation of the characteristics of the carbon bed atomizer for directly analyzing liquid samples.

The advantages of the direct analysis of liquid samples were manifold: a) errors due to sample manipulation were eliminated, b) possible errors due to sample losses as occurred in electrothermal atomizers were eliminated, and c) the times required for analysis were greatly reduced by elimination of preparative steps.

2. Experimental and Discussion: The first experiment undertaken was the determination of the blank value for cadmium in the deionized water, to determine if the large background atomic absorption signal was due to inefficient cleaning of the water, or was merely an indication of extreme sensitivity of the atomic absorption technique.

The deionized water was prepared as follows: distilled water from the Coates Laboratory distilled water system was re-

distilled from a fused silica still. The re-distilled water was filtered through an adsorption column, two research-grade mixed bed deionizing columns and stored in a polyethylene container. Immediately before use the water was passed through a Puritan deionizer-micron filter unit. In spite of these purification steps, the deionized water gave a large background atomic absorption signal.

The calibration attempts using the platinum loop liquid injector and the direct drop liquid injector had already provided sufficient information to perform a "standard addition" determination of the quantity of cadmium contained in the deionized water. As shown by Figure 47, the extrapolation of curves obtained by both calibration techniques indicated the same value for the cadmium content of the deionized water, 5×10^{-4} micrograms per milliliter or 5×10^{-10} grams per milliliter. The detection of such a low cadmium concentration indicated that the atomic absorption technique was extremely sensitive. However, the large absorption signal for this highly purified water offered an obstacle to analysis because of the large blank signal. Unfortunately, the laboratory was not equipped with the clean-room facilities necessary to carry out the ultra-purification procedures to further reduce the blank.[81] To use the "impure" water for analytical work, it was necessary to reduce the sample size to bring the deionized water signal to a reasonable level.

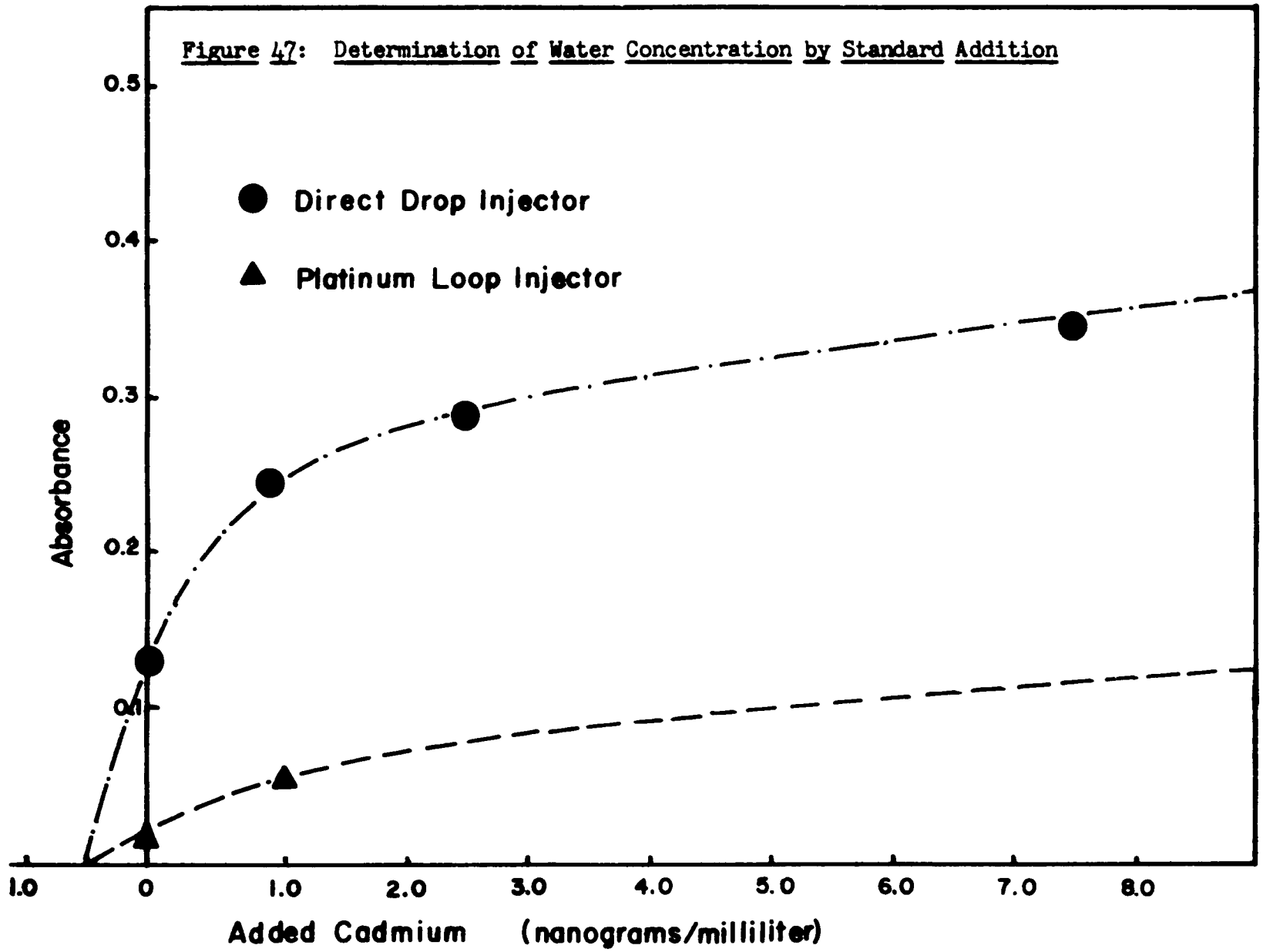


Figure 47: Determination of Water Concentration by Standard Addition
Direct Drop Injector
Platinum Loop Injector
Absorbance
0.5
0.4
0.3
0.2
0.1
-1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
Added Cadmium (nanograms/milliliter)

Unfortunately, it proved impossible to inject quantities smaller than four microliters onto the carbon bed with any degree of precision using the Hamilton syringe. This development brought about the modification and use of the Drummond Microdispenser described in the Equipment Section.

In any atomic absorption system there existed the possibility of chemical interferences, which could result in the observation of a different absorption signal for equal concentrations of metal in different matrices. Such chemical interferences were usually the result of refractory compounds which could not be easily reduced to the free atomic state. In the case of easily excited atoms, there existed a second type of interference; the increase of neutral metal atoms by other easily ionized elements (i.e. the effect of potassium on sodium determination). Because of the low atomization temperature, the contribution from ionization interference would be negligible. For that very reason, however, the formation of refractory compounds might be important.

To test for chemical interferences, standard solutions of 1000 ppm of: $B_4O_7^{=}$, ClO_4^{-}, $MoO_4^{=}$, $SiO_3^{=}$, $TeO_3^{=}$, VO_3^{-}, $WO_4^{=}$, NO_3^{-}, F^{-}, Br^{-}, Cl^{-}, and I^{-} were made up from their sodium salts after the method suggested by West.[82] All of the 1000 ppm solutions were tested for cadmium contamination to see if they contained cadmium levels significantly above the deionized water blank. All of the solutions showed such contamination. However, it was felt that a 10^3 dilution with deionized water would reduce the contribution from such contamination to negligible levels.

Standard solutions for interference studies were prepared to contain 1 ppm of the interfering anion and 1 ng/ml. of cadmium (i.e. a 100 fold excess of the interfering anion) Ten injections of each solution were made onto the carbon bed. The results of the study are listed in Table 3.

No interferences were noted for any of the above listed anions except $ClO_4^=$ and $B_4O_7^=$, which resulted in 15 % and 45% decrease of absorption signal respectively. This information was encouraging in that it showed the carbon bed atomizer to be relatively free from chemical interferences in cadmium analysis.

The interference studies solutions were also tested for molecular absorption using the deuterium lamp. No molecular absorption was found, thus indicating that the anions tested did not contribute significantly to molecular absorption. However, there was still the possibility that such molecular absorption might occur for higher anion concentrations.

Table 3

Chemical Interferences on Cadmium Determination

Interferant	Atomic Absorbance *
$B_4O_7^{=}$	0.12
ClO_4^{-}	0.17
$MoO_4^{=}$	0.[illegible]
NO_3^{-}	0.23
$SiO_3^{=}$	0.19
$SO_4^{=}$	0.20
$FeO_3^{=}$	0.19
$VO_3^{=}$	0.20
$WO_4^{=}$	0.20
F^{-}	0.21
Cl^{-}	0.20
Br^{-}	0.20
I^{-}	0.21

*Each absorbance value is the average of ten injections, and the error is estimated as plus or minus 0.02 units.

F. Direct Determination of Cadmium in Seawater

1. Introduction: Seawater was one of the more difficult samples to analyze by atomic absorption spectroscopy or any other technique because of its high salt content. The high salt content was a major interference in all trace metal analyses because it required extensive pre-treatment in order to perform analyses. The analysis of seawater was quite important to establish natural levels of heavy metals in the oceans. This information was of major interest to the oceanographer, geologist, and pollution control official. The difficulties encountered with the determination of heavy metals in seawater by atomic absorption stemmed from two sources: a) the complexity of the matrix, which caused severe chemical interference effects, and b) the high salt content caused clogging of burners in flame atomic absorption, and high molecular background in electrothermal atomic absorption. Another difficulty in the use of electrothermal atomizers that stemmed from the high salt content was that the temperature necessary to volatilize the species causing molecular absorption (i.e. NaCl) were higher than the temperatures required for atomization of the more easily reduced metals (for example: cadmium, mercury, and thallium).[83]

If it proved possible to analyze seawater directly using the carbon bed atomizer, it would be possible to analyze almost any other aqueous sample, because seawater was one of the most difficult to analyze.

A seawater sample was made available through the courtesy of Texa Instruments.

2. Experimental and Discussion: In an initial attempt to determine the cadmium concentration of seawater, several 4 microliter injections were made onto the carbon bed by the direct drop technique. In every case, the absorption trace looked like that shown in Figure 48a, indicating either that the cadmium concentration was too high and the system was being "flooded" with cadmium, or that the molecular absorption due to the high salt content of sea water was too great. To differentiate between these two possibilities the atomic line source was replaced by the deuterium lamp and the molecular absorption characteristics of the sea water samples determined. The results of the molecular absorption studies were shown in Figure 48b, which indicated that the molecular absorption was high, but was not large enough to account for the large signal observed with the hollow cathode. Hence, seawater exhibited a large net atomic absorption signal.

It was felt that a dilution of the sample with deionized water would bring both the atomic and molecular signals into a useable analytical range, so a portion of the seawater sample was diluted 9:1 and the atomic and molecular signals re-determined. The results of the analysis after dilution were shown in Figure 49a and 49b. From the atomic absorption traces, it was apparent that the "flooding" of the system had been eliminated, and that the molecular absorption signal had been reduced to a value of only 10% absorption. A comparison of the absorbance value with the calibration curve and subsequent calculation indicated that the seawater sample contained 7×10^{-2} micrograms per milliliter cadmium.

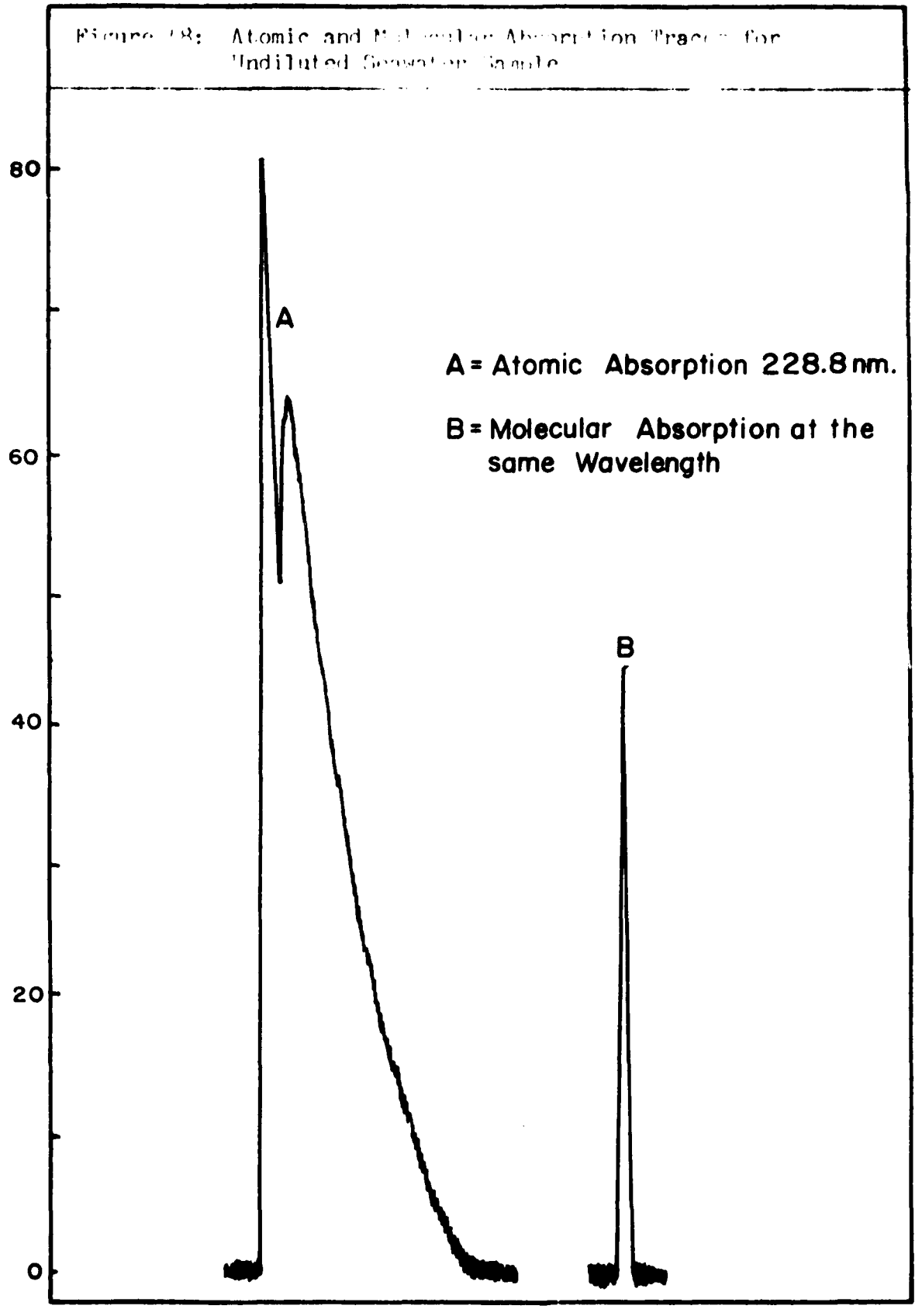
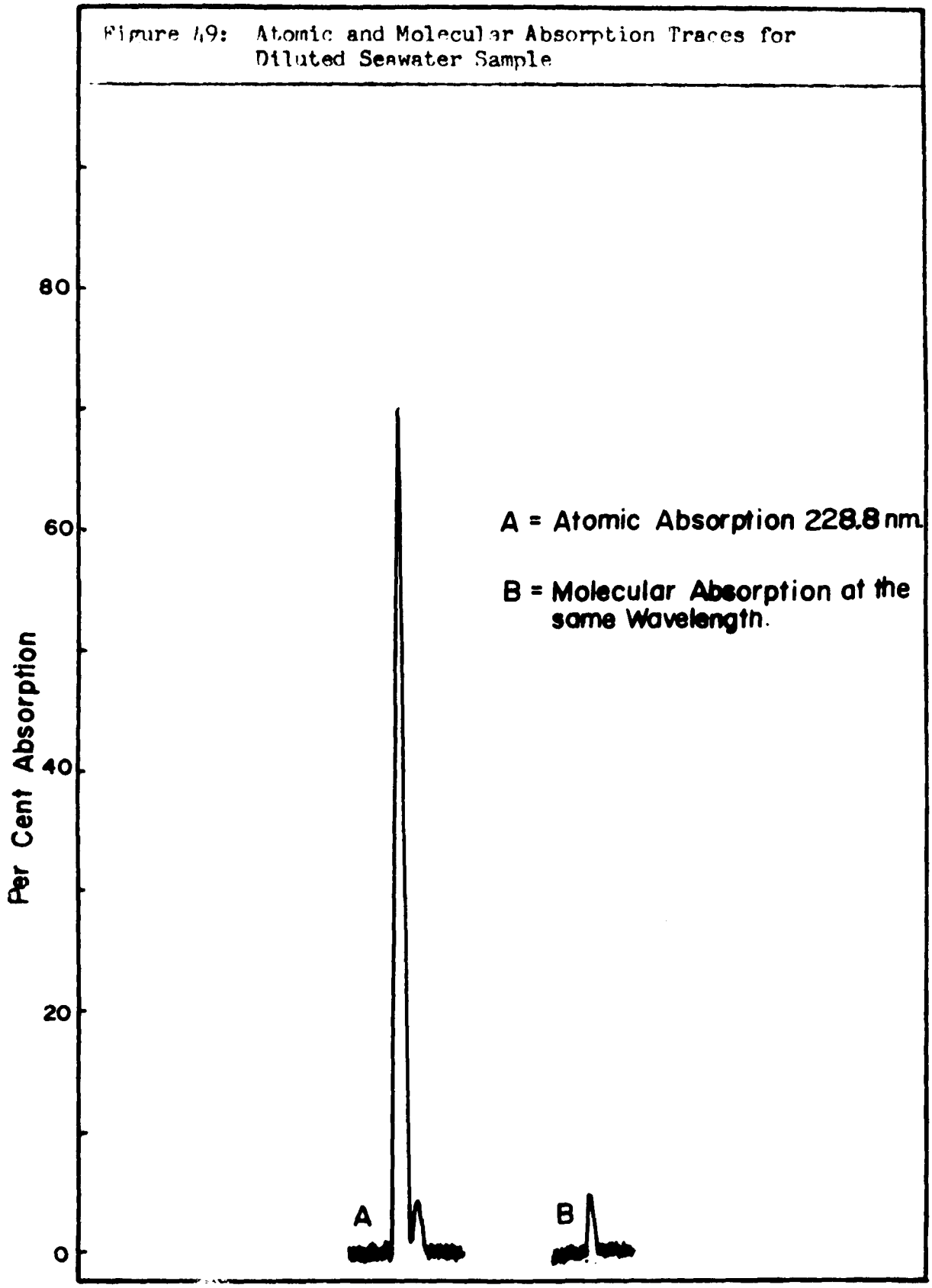

80
60
40
20
0
A
B
A = Atomic Absorption 228.8 nm.
B = Molecular Absorption at the same Wavelength

Figure 49: Atomic and Molecular Absorption Traces for Diluted Seawater Sample



G. Direct Determination of Cadmium in Urine:

1. Introduction: Urine was an excellent example of a typical biological fluid. The obstacles that it presented to the analyst were extreme. Not only did they include all of the difficulties due to a high salt content (as for seawater), but urine presented the extra complication of a high organic content. For the same reasons that it proved difficult to analyze seawater, it was not possible to analyze urine directly. Many different sample treatment schemes have been formulated, [84, 85] all of these presented the opportunity for the introduction of errors.

The analysis of urine for the determination of trace metals was of importance in clinical studies and was necessary to determine the health effects of environmental pollutants. [86]

The carbon bed atomizer had demonstrated the capability of analyzing seawater directly. It was thus a possibility that urine might also be analyzed directly. Hence, a study of the possibilities of direct determination of cadmium in urine was undertaken.

2. Experimental and Discussion: Using the direct drop technique, 4 microliter urine samples were dropped directly onto the carbon bed. The results of the undiluted urine sample are pictured in Figure 50a. The absorption trace showed the trailing effect which was indicative of a "flooded" system. As in the case of the seawater samples it was necessary to determine how much of the absorption signal was actually due to cadmium and how much was due to molecular absorption or scattering. Hence, the hollow cathode

Figure 50: Atomic and Molecular Absorption Traces for Undiluted Urine Sample

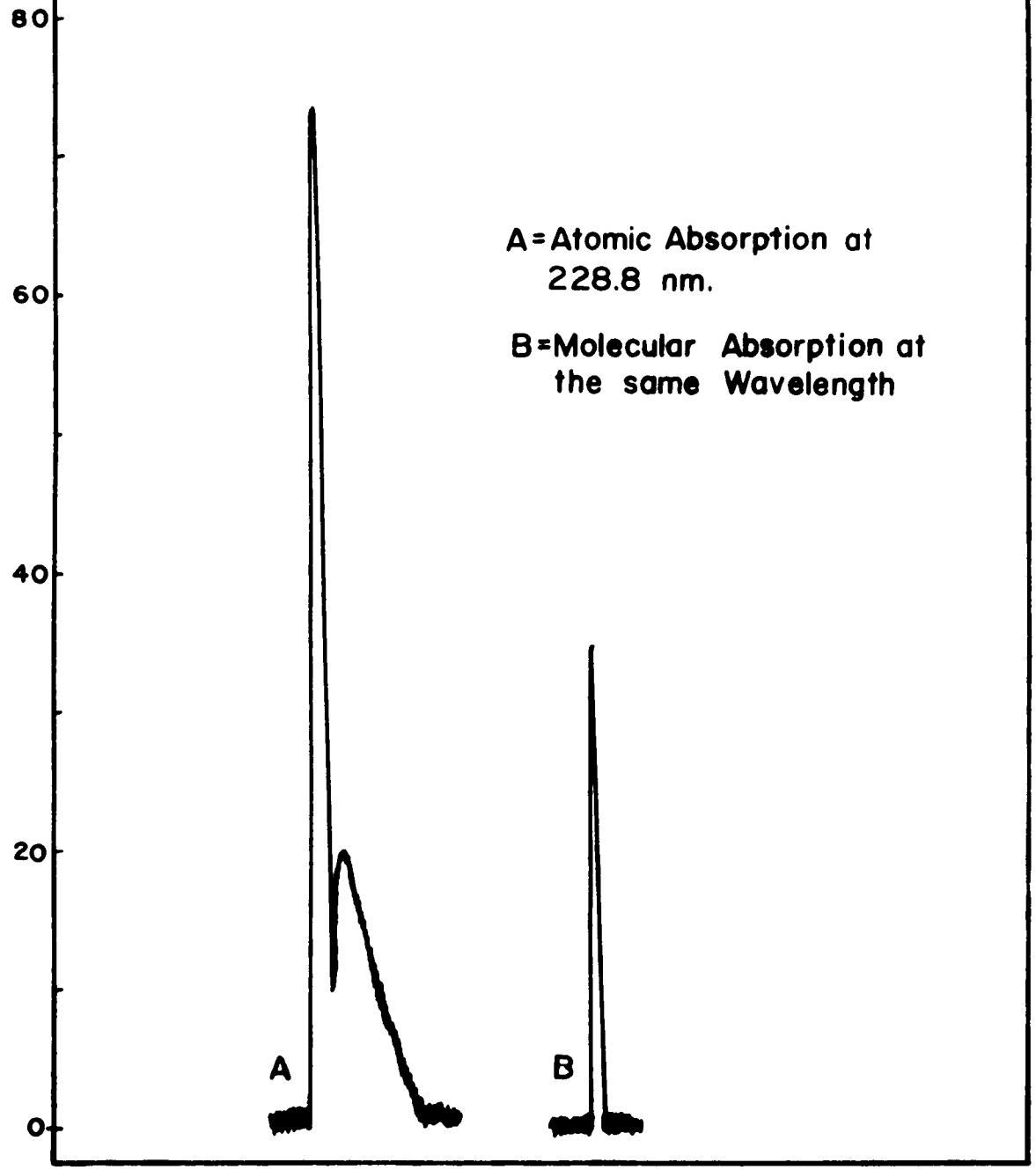
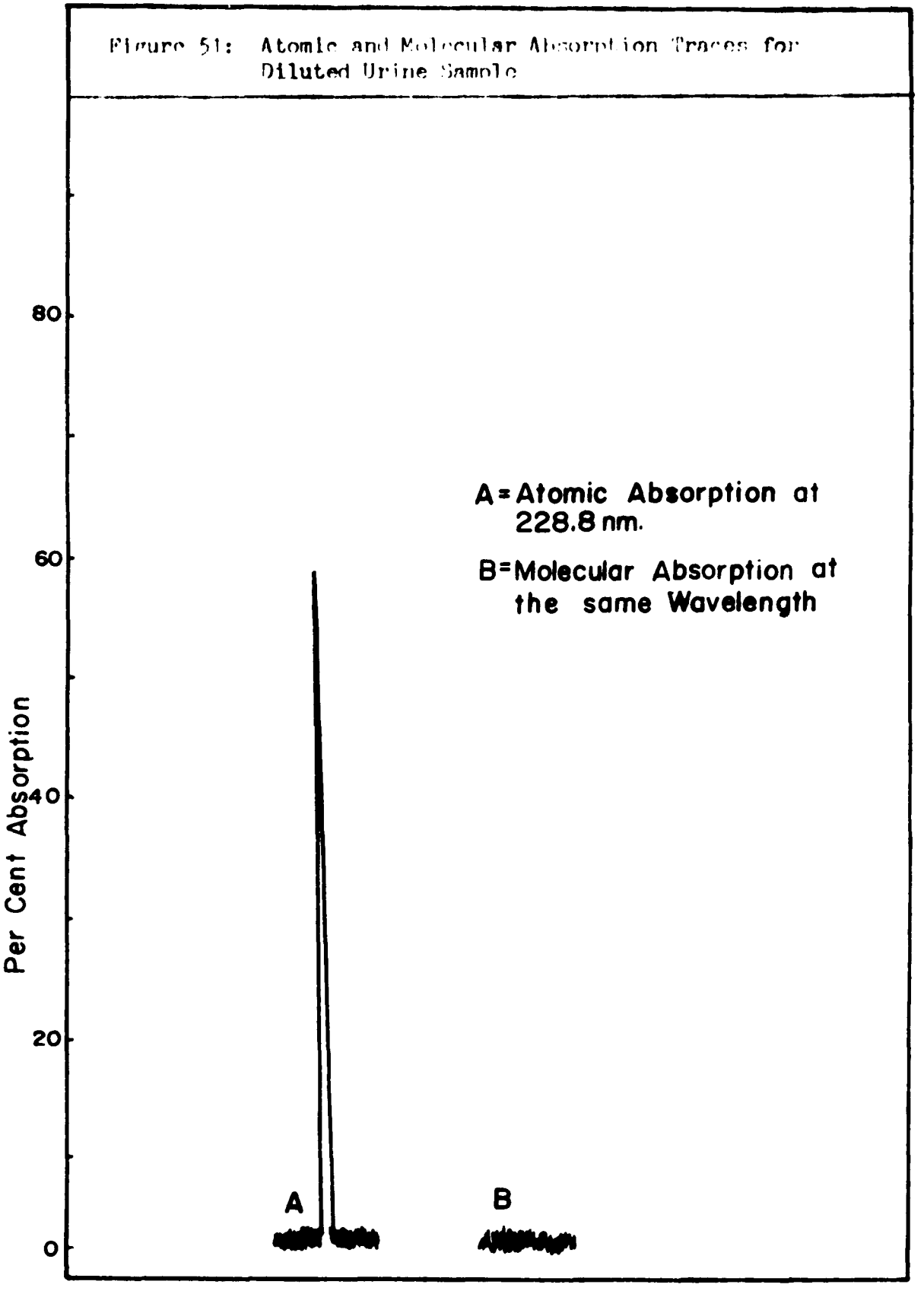


Figure 51: Atomic and Molecular Absorption Traces for Diluted Urine Sample



was replaced by the deuterium lamp and the injections of undiluted urine repeated. The results of the molecular absorption study were shown in Figure 50b . A comparison of the atomic and molecular absorption signals indicated a large net atomic absorption signal. It was not possible to obtain useable information with the undiluted urine sample because the concentration of the sample was too great. It was felt that a dilution with deionized water would overcome these difficulties as it had for seawater.

A portion of the urine sample was therefore diluted 9:1 with deionized water, and injected onto the carbon bed. The comparative illustration of atomic and molecular signals were shown in Figure 51a and 51b. The data indicated that the atomic signal had been reduced to an analyzable level, and that molecular absorption had been completely eliminated.

A comparison with the calibration curve and subsequent calculation indicated that the original urine sample contained 1×10^{-2} micrograms per milliliter of cadmium.

H. Micropipette Modification

1. Introduction: In all of the preceeding analyses of liquid samples, the Hamilton syringe was used for injection. The precision using the syringe was 10% r.s.d. However, it was felt that the precision of analysis could be improved by increasing the precision of injection. The error introduced by injection was felt to be the major source of imprecision.

The problem could be overcome by the use of a device that possessed the capability of mechanical positive displacement of the sample. One such device was the Drummond Microdispenser. One of these devices was purchased from Drummond Scientific Corporation and used for injection of liquid samples;

2. Experimental and Discussion: As delivered, the micropipette proved totally unsatisfactory. The large diameter of the glass barrel caused excessive drop "hang-up". Because of this, it proved impossible to inject liquids onto the carbon bed. The difficulties were overcome by a minor modification of the device (described in Equipment Section). By means of this modification, the Microdispenser was converted to an air-displacement device.

In operation, the plunger was depressed to one of the pre-calibrated stops, and the glass barrel inserted into the liquid to be sampled. Releasing the pressure caused the spring-loaded plunger to draw the requisite volume of solution into the pipette barrel. Depressing the plunger again ejected the solution from the pipette. There was no possibility of liquid hangup, because a small

volume of air was automatically retained between the plunger and the liquid which forced all of the liquid out of the barrel. The use of this device greatly improved the precision of liquid injection, resulting in a precision of 4 % r.s.d. The data obtained in this investigation were given in Table 4.

TABLE 4

DRUMMOND MICRODISPENSER PRECISION DATA*

	Run 1		Run 2
	0.487		0.4[illegible]
	0.521		0.4[illegible]
	0.491		0.482
	0.547		0.492
	0.491		0.492
Average	0.503	Average	0.4[illegible]
	0.50 ± 0.02		0.49 ± 0.01

*Sample Size 0.04 micrograms/ milliliter
Data expressed as absorbance

I. Direct Analysis of Solid Samples:

1. Introduction: The analysis of solid samples was plagued by all of the difficulties outlined for liquid samples, together with the added problem of sample dissolution. All of these sample pretreatment steps introduced possililities for the introduction of error.

There were many solid samples which were of interest in studies of trace metals. In order to analyze these by atomic absorption, complicated pretreatment schemes were usually necessary to render them into liquid form. Typical examples and treatment were as follows: biological tissues-nitric or perchloric acid digestion to destroy organic matrix,[87] soil samples-hydrofluoric acid digestion to remove siliceous material,[88] filter materials-ashing and/or acid digestion to destroy matrix prior to analysis for the filtered materials.[89] All of these pretreatment routines, with their attendent possibilities for error, could have been eliminated by the availability of a technique capable of direct analysis.

It was felt worthwhile to investigate the possibility of direct analysis of solid samples on the carbon bed atomizer, since it had shown its effectiveness for direct analysis of liquids without any sample pretreatment.

Two sample types were investigated. The first of these was filter paper. This material is basically cellulose and thus possesses many of the characteristics of natural products which are important in biological and environmental studies.

These included: plant tissues, molds, fungi, foods, etc. In addition, filter paper is possibly the most widespread means for gathering particulate samples from the atmosphere, especially for automated sequential sampling. It would be extremely advantageous to analyze the particulate materials directly on the filter paper without extensive pretreatment.

The second sample tested was polyethylene, for a number of reasons: a) polyethylene was representative of most of the available synthetic polymers in its combustion characteristics in the atomizer, b) because of its purity it was widely recommended as a material for sample containers in trace analysis, c) it was available for use in a great variety of forms, d) it was a widely used material for biological and medical applications, and e) polyethylene was most suitable for fabrication of small containers for direct analysis of solid materials as dusts or powders by providing a sample vehicle that could be introduced directly into the atomizer.

2. Experimental and Discussion:

A. Direct Analysis of Filter Papers

Several filtering materials were available for testing. These different filter types are listed in Table 5. Trace element analyses of the more common heavy metals were provided by the manufacturers for some of these filters. The analysis data are listed in Table 6. These impurity levels were based on a filter disc of 47 mm. diameter. The particular size chosen for experimental work was a disc of 6 mm. diameter. This size was chosen for two reasons:

Table 5

Available Filter Materials

Millipore HAWP

Whatman 1

Whatman 50

Whatman 40

Whatman 44

Reeve Angel 201

Reeve Angel 202

Table 6

Trace Element Levels (ppm)

Element	Qualitative Grades	Quantitative Grades	Hardened Grades
Aluminum	3.	3.	1.
Boron	0.5	0.3	0.2
Calcium	127.	13.	39.
Copper	1.	0.5	0.5
Iron	9.	2.	2.
Lead	0.2	0.1*	0.1*
Magnesium	7.	2.	2.
Mercury	0.1	0.05	0.05
Potassium	5.	0.5	0.5
Sodium	86.	8.	5.
Zinc	2.	0.4	0.5

* Less than

(Whatman 1 = Qualitative; Whatman 40, 44 = Quantitative; Whatman 50 = Hardened)

Data from manufacturer's literature.

a) it was smaller than that size observed to cause "flash-back" upon combustion in the atomizer, b) a mechanical punch was available in this size.

In the first experiment, it was desired to determine the background levels of lead in the various media. Lead was chosen as the element to be determined because it was a common pollutant and there was interest in performing particulate filtering experiments in this laboratory. Consequently, 6 mm. diameter discs were dropped onto the carbon bed and their lead content determined. The results of this experiment were given in the first column of Table 7. Subsequently, the lead hollow cathode was replaced by the deuterium broadband source, and the molecular absorption of the different filter papers determined. The molecular absorption data were also listed in Table 7.

The data showed that molecular absorption by untreated carbon filters was negligible. But the atomic absorption blank due to lead was so great at the 217.0 nm. resonance line as to preclude any analysis using filter papers as a sample vehicle.

A qualitative study using the 283.3 nm. resonance line showed the same results, even though the resonance line was less sensitive. Background contamination was too great for the use of filter papers as an analytical medium.

Another qualitative study performed at the 261.4 nm. lead resonance line showed minimal background contamination for lead, but as this line is approximately one hundred times less sensitive

Table 7

Absorbance Signals for Various Filter Papers

Paper	Molecular Absorbance*	Atomic Absorbance**
Millipore HAWP	0.01	0.74
Whatman #1	0.04	1.05
Whatman #40	0.06	1.05
Whatman #44	0.01	0.73
Whatman #50	0.03	0.98
Reeve Angel 201	0.03	1.10
Reeve Angel 202	0.08	1.10

* Molecular Absorbance using Deuterium Lamp

** Atomic Absorbance using Lead Hollow Cathode

than the 217.0 nm. line,[90] much of the main advantage of non-flame analysis (i.e. high sensitivity) was lost.

These experimental results, while discouraging from the standpoint of practical analyses using untreated filter papers, were indicative of the high sensitivity of the carbon bed atomizer for lead. As an example, Millipore filter discs were said to have a lead blank for 47 mm. diameter disc which was undetectable by standard flame atomic absorption. Yet for a disc with only one-eighth the diameter, the carbon bed atomizer studies indicated full scale deflection. Here indeed was sensitivity.

To use filter paper as a sample vehicle, it was necessary to reduce the lead blank levels. It was decided to try to leach the lead contamination out of the filter papers with different acids, organic chelating agents, or complexing agents. Samples of Whatman 44 filter paper were placed in small polyethylene vials and leached for a period of one hour. The leached papers were then rinsed three times with solvent, dried under clean, filtered air, and analyzed on the carbon bed atomizer. The leaching agents used were: deionized water, carbon tetrachloride, 10% nitric acid-deionized water, ammonium acetate-deionized water, 10% hydrochloric acid-deionized water, and dithizone in carbon tetrachloride. The results of the atomic absorption and molecular absorption studies for the leached filter papers were listed in Table 8. The leaching efficiency, in decreasing order, was: a) nitric acid-deionized water, b) carbon tetrachloride, c) dithizone in carbon tetrachloride, d) ammonium

Table 8

Lead Removal by Leaching
From Whatman 44 Filter Paper

Sample Leach	Atomic Absorbance*	Molecular Absorbance**
Unleached	1.78	0.01
Deionized Water	1.66	0.05
Nitric Acid	0.29	0.05
Ammonium Acetate	1.36	0.03
Carbon Tetrachloride	0.74	0.07
Dithizone (in CCl_4)	1.02	0.03

* Atomic Absorption Signal

** Molecular Absorption Signal

acetate in deionized water, and e) deionized water only. The combination of agitation and hydrochloric acid was destructive to the filter paper, so no determination was possible when this technique was used. The results for carbon tetrachloride and dithizone in carbon tetrachloride were puzzling, indicating as they did that the carbon tetrachloride was more effective than dithizone in carbon tetrachloride, as dithizone was an excellent complexing agent for lead and was used in many solvent extraction techniques.[91] One possible explanation was that the dithizone was capable of leaching all the lead from the container walls, thus contaminating the leaching solution and reducing its lead-removing capabilities. The molecular absorption studies indicated no change in molecular absorption of the filter paper after leaching.

These studies showed that the most effective leaching agent used in these studies was a nitric acid solution. Although the blank lead level was reduced from 1.78 absorbance to 0.29 absorbance, the reduction was insufficient to make maximum utilization of the available sensitivity of the atomic absorption technique. It would, however, have been possible to obtain useful analytical data with such a blank lead level.

There were several possibilities for further reducing the lead blank: a) successive leaches with the fresh nitric acid mixture, b) leaching with an EDTA solution, c) leaching with a more dilute hydrochloric acid solution. In any event, the effectiveness of leaching as a means of contaminant removal at trace levels had been demonstrated.

b) Direct Analysis of Polyethylene:

A study was undertaken to determine: a) the degree of trace metal impurity in polyethylene, and b) the best technique for removing trace metal contamination. Lead and cadmium were chosen as the elements to be determined, since the instrument was already set up to determine these elements.

Samples of polyethylene were cut from Intramedic Medical Formulation PHF polyethylene tubing. The dimensions of the tubing were 0.045 inches inside diameter and 0.062 outside diameter. The tubing was cut into samples of lengths 0.2 cm., 0.5 cm., 0.8 cm., or 1.0 cm.

To determine the blank levels, samples of each length of polyethylene were injected onto the carbon bed. Measurements of lead atomic absorption were taken using the 217.0 nm. resonance line. The atomic absorption data were given in Table 9. The data indicated that the lead blank signal was so great as to preclude the possibility of using unleached polyethylene as a sample vehicle. Indeed, for samples longer than 0.5 cm., complete absorption of hollow cathode radiation was observed.

It was also necessary to determine the contribution to absorption made by molecular species. The lead hollow cathode was replaced by a deuterium lamp, and the absorbance monitored over the spectral bandpass at 217.0 nm. These data were also given in Table 9. The molecular absorbance due to combustion products was small, and of the same magnitude as the molecular absorbance of water and filter paper under the same conditions.

Table 9

Lead Contamination of Polyethylene

Measured at the 217.0 nm. Resonance Line

Sample Size	Atomic Absorbance	Molecular Absorbance
0.2 cm.	1.03	0.01
0.5 cm.	1.28	0.02
0.8 cm.	*	0.0[illegible]
1.0 cm.	*	0.03

*indicates total absorption of hollow cathode radiation

It was not possible to assign concentration values to the lead absorbances as they were too great.

In an effort to reduce the lead background, 0.5 cm. lengths of polyethylene were soaked in 10% nitric acid for twenty minutes, then rinsed with deionized water and dried in clean air. This procedure was repeated for different polyethylene samples using hydrochloric acid and dithizone in carbon tetrachloride. In the case of samples leached with the dithizone solution, the final rinse was carbon tetrachloride rather than deionized water.

Samples of the leached polyethylene were injected into the atomizer, and the lead absorbance at 217.0 nm. measured (see Table 10). The data indicated that the acid leaches had greatly reduced the lead levels, and that hydrochloric acid was a more effective leaching agent than nitric acid. The dithizone solution was ineffective in removing lead contamination. These results were consistent with those obtained in the study of removal of lead contamination from filter paper.

To determine the value of successive leaches on cleaning efficiency, samples of 0.5 cm. polyethylene were leached for one and two hours with nitric acid, rinsed with deionized water, and dried under clean air. Other samples were washed with hydrochloric acid in the same manner. After all the samples had dried, they were individually injected into the carbon bed. The data for lead absorbance of these samples was presented in Table 11. The data indicated that successive leaches were quite effective in removing contamination, and that the use of hydrochloric acid resulted in a much more effective lead removal. A comparison of the nitric acid

Table 10

Lead Removal from Polyethylene *

Sample Leach	Atomic Absorbance+	Molecular Absorbance ++
Nitric Acid	0.56	0.02
Hydrochloric Acid	0.39	0.02
Dithizone (in CCl_4)	**	0.03
Blank	1.67	0.02

*Sample size = 0.5 cm.

**Indicates total absorption

+ Atomic Absorption

++ Molecular Absorption

leaching data obtained in this experiment, and that obtained for the single 20 minute leach (see Table 9) indicated that a long leaching time was not as effective as a number of short successive leaches for removing lead contamination. Another interesting point was the change in the scatter of absorbance signals with successive leaches. As the absorption signals became smaller, the variation in signal between samples decreased by 60%. This data indicated that the lead contamination was unevenly distributed over the polyethylene and approached a limiting value with successive leaches. In view of the ease with which the contamination was removed, and the fact that variation in signal decreased with successive leaches, it seemed likely that the lead contamination was on the surface of the polyethylene.

An investigation into the cadmium contamination of polyethylene was also carried out. Samples of polyethylene 0.5 cm. long, were injected onto the atomizer bed, and the cadmium atomic absorption measured at the 228.8 nm. resonance line. Such injections resulted in almost total absorption of the hollow cathode radiation.

Obviously, it was necessary to find some means to remove the cadmium contamination. Samples of the polyethylene were soaked in a 6% hydrofluoric acid solution three times in succession for periods of one hour each. After each leaching period, some of the polyethylene samples were removed from the washing solution, rinsed with deionized water, and dried under clean air. Upon completion of all leaching, samples from each successive leach were injected onto the carbon bed, and the cadmium absorbance measured. The results of

Table 11

Effect of Successive Leaches upon Lead Removal

Leach Number*	Atomic Absorption from Samples Leached a) in Nitric Acid	b) in Hydrochloric Acid
0	1.29	1.29
1	0.61	0.23
2	0.22	0.04

* time allowed for each leach was one hour.

(Note the progressive decrease in lead levels with successive leaches, and the greater effectiveness of hydrochloric acid in lead removal.)

Table 12

Cadmium Removal from Polyethylene by Leaching with Hydrofluoric Acid

Leach Number*	Atomic Absorbance
0	1.15
1	0.27
2	0.06
3	0.06

*time allowed for each successive leach was one hour.

(Note complete removal of cadmium after only two washes.)

the experiment were listed in Table 12. The data showed a drastic decrease of absorbance by cadmium after only one leach. Since the results of the second and third leaches showed no further decrease, it was concluded that all leachable cadmium had been removed in the first wash. The data thus indicated that the majority of the cadmium contamination was on the surface of the polyethylene, and that leaching was ineffective in removing interior contamination.

Using the acid leaching techniques, it was possible to remove the surface contamination from polyethylene. The ability to clean the plastic effectively opened the possibility of using such plastics as sample containers for the direct analysis of powder samples.

The data for lead and cadmium in both leached and unleached polyethylene were summarized in Table 13. Due to the great fluctuation in absorbance signal caused by the uneven distribution of the surface metal content, the values for the unleached samples indicate the lowest observed metal content.

Table 13

Lead and Cadmium Levels in Polyethylene

Element	Unleached*	Leached
Cadmium	1.8×10^{-9}g.	1.2×10^{-11}g.
Lead	5×10^{-8}g.	5×10^{-10}g.

*represents lowest level due to great fluctuation of lead and cadmium values in unleached polyethylene

IV. CONCLUSIONS

A. Factors Affecting Atomization and Atomic Absorption Signal

The basic factors affecting atomization efficiency were shown to be temperature, flow rate, carbon bed depth and carbon size.

In order to measure the effect of temperature upon atomization efficiency, it was first necessary to determine the factors affecting temperature. These were shown to be: total radio-frequency power coupled into the carbon, the frequency of the generator, the size of the individual carbon pieces constituting the atomizer charge, and the total quantity of carbon in the charge (expressed as bed depth). Bed temperature was shown to increase with the output power of the radiofrequency coil, and reach a maximum value of 1500° C. The limitation preventing attainment of higher temperature was the stability of the material comprising the absorption cell and not the ability of the generator to couple more power into the carbon. The temperature depended on the coupling between the radiofrequency coil and the carbon pieces. The effectiveness of coupling depended on carbon size and frequency of the generator. With decreased carbon size, the frequency must be increased correspondingly to attain high temperature. At constant frequency, maximum temperature was attained for pieces of carbon 8 mm. in length by 6 mm. in diameter. A similar effect was shown to occur for the depth of the carbon bed. The temperature was a maximum for a carbon bed depth of 50 mm.

Temperature was shown to increase atomization efficiency

up to a maximum of 1350° C. No further increase of atomization efficiency with increased temperature was observed at higher temperatures for cadmium.

Flow rate was shown to exhibit an increase in atomization efficiency with decreasing flow rate. Such an increase was observable on the basis of peak area, because decreasing flow rate also decreased peak height.

Studies of the effect of the depth of carbon bed on atomization efficiency indicated a slight increase of atomization efficiency with bed depth. Such an effect would not decrease atomizer efficiency significantly during operation as the depth of carbon bed decreases only 12 mm. over a period of four hours.

Carbon size studies showed an unexpected increase in atomization efficiency with increasing carbon size, in spite of the expected effect of an increased surface area for reaction with decreased carbon size. The effect might have been due to a broadening of the absorbance peaks, but could not be investigated further as no means of effectively measuring peak area was available.

A memory effect was indicated for large concentrations of cadmium (10^{-6} grams) which was removed by repeated injections of water.

B. Factors Affecting Molecular Absorption Signal in Carbon Bed Atomic Absorption

The factors affecting molecular absorption signals in the carbon bed were shown to be flow rate, temperature, carbon depth, species injected, and spectral region.

Molecular absorption was shown to be highly dependent on flow rate of air through the atomizer cell. Decreasing molecular absorption was observed with decreasing flow rate. This effect was attributed to the improved combustion of solvent to carbon monoxide and hydrogen in the carbon bed.

The temperature was shown to have no effect on molecular absorption over the temperature range 1000° to 1500° C.

Studies on depth of the carbon bed indicated that molecular absorption increased for smaller carbon beds. Such an effect was attributed to incomplete combustion of solvent to carbon monoxide and hydrogen. The effect was similar to that observed for flow rate.

Different species absorb over different wavelength ranges. Consequently, interference due to molecular absorption was a function of the chemical composition of the interferant. In general, the molecular absorption was more severe between 200 nm. and 240 nm. In any event, molecular absorbance never exceeded 0.10 absorbance units and could have been easily corrected by a deuterium lamp background corrector.

The possibility of sample losses from carbon during preheating cycles was observed directly, and the possibilities for error introduced by use of such cycles in reduction of molecular absorption was demonstrated.

c. Observation of Atomic Absorption Signals from Ambient Air:

In order to obtain quantitative results from ambient air signals, it was necessary to have a reference material, that is, pure air. Several systems for the purification of air and introduction

of ambient and clean air into the atomizer were designed and tested.

Using a vacuum-flow system, atomic absorption signals were obtained for sodium, potassium, lead, arsenic, selenium, copper and zinc. The flow system used in the observation of these signals was not entirely satisfied and was modified. The modified flow system was used to measure atomic absorption signals for cadmium in the ambient air.

D. Calibration Methods for Atomic Absorption

Several systems were tried for calibration of the spectrophotometer for air analysis. These included: high temperature volatilization, impregnated carbon pellets, platinum loop liquid injection and direct drop liquid injection.

The high temperature volatilization technique proved unsatisfactory due to preferential volatilization of metallic impurities, decomposition of calibrating materials, and a lack of sufficient temperature control.

Impregnation of liquid standard solutions onto carbon pellets and injection into the atomizer of these pellets was also unsatisfactory. The technique suffered from very poor precision, probably due to differences in carbon porosity.

The precision obtained when the platinum loop injector was used was sufficient to obtain calibration data. However, the results indicated a failure of the technique to fulfull the conditions necessary to relate liquid solution concentration to ambient air concentration.

Of the procedures tested, the direct drop technique was the most reliable. It gave the best precision and was the most versatile of all the techniques tried.

In order to relate the liquid concentration to an ambient air signal, it was necessary that the injection technique fulfill certain qualifications. These qualifications were discussed and found to be best fulfilled by the direct drop technique.

E. Direct Analysis of Water Samples

The direct drop injection technique opened up the possibility of analyzing liquid samples on the carbon bed atomizer. Using the technique, the blank cadmium concentration in deionized water was measured.

Direct analysis of water samples proved quite simple, and an investigation into the chemical interference effects of various anionic species showed the technique to be relative free from interferences in cadmium analysis.

F. Direct Determination of Cadmium in Seawater

Seawater was normally a very difficult sample to analyze because of its high salt content, but it proved possible to analyze seawater for cadmium with only a dilution step.

The possibility of a high molecular background due to the high salt content was investigated, and the molecular absorption was found to be within acceptable limits.

G. Direct Determination of Cadmium in Urine

Like seawater, urine was normally a difficult sample to analyze, and for many of the same reasons. Urine had not only a high salt content, but a high organic content as well. As was the case with seawater, the urine sample was too concentrated and a dilution was necessary to determine the cadmium content. Upon dilution, the urine sample proved quite easy to analyze.

An investigation into the molecular background absorption of the urine sample indicated that molecular absorption presented no problem in the analysis.

The capability to analyze urine directly for the determination of trace metals should be quite useful for clinical analysis and for the determination of the health effects of metallic pollutants.

H. Micropipette Modification

In the direct drop technique, samples were injected with a Hamilton microliter syringe. Although acceptable precision was attained, it was felt that the precision could be improved.

A Drummond Microdispenser was purchased, and after slight modification into an air-displacement injector, proved capable of increasing the precision with which samples could be injected into the atomizer.

I. Direct Analysis of Solid Samples

From the difficult samples of urine and seawater, it was only a step to the analysis of solid samples. Analyses were carried out by merely dropping the samples directly onto the carbon

bed and monitoring the absorption signal. Analyses of filter paper and polyethylene proved that, although it was possible to analyze them directly, the metal blank signal was quite high. Investigation of molecular absorption showed it to be negligible.

In order to use filter paper or polyethylene as sample vehicles for other solid samples, it was necessary to reduce the high blank atomic absorption signal. Various leaching schemes were tried to reduce the metal blank signal, with an acid leach technique proving the most effective. Cadmium was best removed by hydrofluoric acid and lead by hydrochloric acid. The leaching technique reduced blank levels sufficiently that analytical results could have been obtained for samples using filter paper or polyethylene as the sample vehicle.

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EXAMINATION AND THESIS REPORT

Candidate: Duane Kent Wolcott

Major Field: Chemistry

Title of Thesis: Methods for the Direct Determination of Heavy-Metal Pollutants in the Environment

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 18, 1973